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HYDROGENATION
OF ALBERTA BITUMEN AND COAL
AT ELEVATED TEMPERATURES AND HIGH PRESSURES

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THE S I S

PARTS I AND II

On the hydrogenation of bitumen from the
bituminous sands of Alberta.

PART III

Preliminary experiments on the liquefaction
of characteristic Alberta coals by hydrogenation at
high pressures and elevated temperatures.

Presented in fulfillment of the requirements
for the degree of Master of Science.

April, 1931.

A. W. SADDINGTON.

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INTRODUCTION.

Alberta's coal fields, bituminous sand deposits and natural gas resources represent three of the world's important supplies of carbonaceous materials (1, 4, 16). Development of these is at present confined to a few coal producing areas and to three gas fields. Among the gas fields being exploited is the Turner Valley area which produces a "wet" gas containing a relatively small amount of naphtha. These gases are stripped of their naphtha content and the remaining dry gas, largely methane, is for the greater part destroyed by burning in the field. Thus, some 60,000 cubic feet of gas are destroyed for each barrel of naphtha recovered. About 75,000,000 cubic feet of gas are used daily in the neighboring cities but this is not more than one eighth of the total gas available. Apart from the Turner Valley field there are in the province many dry gas wells, at present capped and conserved, awaiting utilization. In 1926 the possible daily production of these dry gas fields was in excess of 400,000,000 cubic feet (2).

An important and promising field for the utilization of natural gas lies in its use as a raw material in chemical industry either directly or as a source of gases more amenable to chemical change. This thesis consists of a report of one such project and a preliminary account of a second.

In view of the availability of cheap and adequate sources of the necessary raw materials an investigation of a process of liquefaction by hydrogenation of Fort McMurray bitumen was initiated in the summer of 1929. Later this reaction was extended to certain typical Alberta coals. From an industrial point of view the processes of hydrogenation of carbonaceous materials depend for success on a sufficient and cheap source of hydrogen. The commercial production of hydrogen from natural gas has been shown to offer no great experimental difficulties.

As witnessed by a tremendous volume of patent literature the hydrogenation or berginization of coals, lignites, tars, etc., has been the subject of much enquiry within the last few years, (9, 14). There has been developed a comparatively successful operating technique. In what follows the particular application of this technique to bitumen and coal is described. Preliminary experiments on the reaction of hydrogen with bitumen at high temperatures and pressures were conducted in an alloy steel autoclave supplied by C. W. Cook and Sons of England.

These experiments showed conclusively that this reaction was possible and resulted in a maximum oil yield of 80%, the remainder going to coke and gas.

Indications were obtained that the process was much superior to cracking under the same experimental conditions by virtue of higher oil yields and a lower coke formation. However, the design of this autoclave did not permit a uniform or even controlled temperature distribution. It was deemed advisable to investigate the process further in a

reaction vessel of more appropriate design. Part II of this paper presents the results obtained with an autoclave more than twice as large, designed to allow an efficient agitation of its contents and not more than a variation in temperature of $10^{\circ}\text{C}.$ over its length. In this manner regions of high temperature and little agitation were eliminated and thermal decomposition to coke and gas minimized. The more precise experiments possible with this apparatus confirmed and extended the original work. Light oils were produced and coke formation altogether suppressed at reaction temperatures up to $425^{\circ}\text{C}.$ in the presence of an active catalyst. The yield of gasoline varied from 20 to 30% and this was largely increased by successive hydrogenation of the oils remaining after the original gasoline had been removed. Lubricating oils and paraffin wax result in considerable amounts by partial hydrogenation of the bitumen. The work points to the use of a continuous system of hydrogenation in an enlarged autoclave which would allow reaction in both gaseous and liquid phases.

LITERATURE REVIEW.

The production of liquid fuels from carbonaceous materials is an acute problem to those countries lacking large petroleum deposits. European countries are particularly unfortunate in their small petroleum resources. The fact that they possess extensive coal fields has lead countries such as Great Britain, France and Germany into research on the possibilities of converting coal or coal tar into the much needed fuel oils. We must look to these countries, then, as the leaders in this particular field of research. One line of attack on the problem has been the action of hydrogen on carbonaceous materials at high pressures and temperatures. Berthelot made the first attempt to hydrogenate coal (11).

He used a saturated hydriodic acid solution as his reaction medium. Working at a temperature of 270°C . over time intervals up to twenty-four hours he was able to convert 60% of the coal to liquid products. However, it was not until fifty years later that this work was reopened by Tropsch (12), who, using a slightly modified procedure involving sealed tubes and the consequent thermal pressure, confirmed Berthelot's findings and also noticed that younger coals were more susceptible to this reaction. He reported from 12 to 70% conversion of the original coal to petroleum like oils. About this time Fischer developed a method using sodium formate as an hydrogenating agent (13). Here, the other soluble hydrogenated products amounted to 45% of the coal in some cases. Pressures as high as fifty atmospheres were reached in this work. Higher pressures to about ninety

atmospheres resulted in only a moderate improvement in the oil yields.

Friederich Bergius was lead by the above work to attempt the direct addition of hydrogen at high temperatures and pressures to a synthetic coal in the structure of which he was much interested, (3). He obtained a petroleum like oil as a result. The process was next applied to heavy hydrocarbon oils and coal. Bergius mixed his powdered coal with a solvent, usually a heavy paraffin oil, and treated it at temperatures varying from 300 to 500°C. at hydrogen pressures up to 200 atmospheres for varying lengths of time. Distillates were obtained amounting to 100% of the original coal. Later this process was put on a continuous basis. Here, the oily suspending medium acquired a new function since it rendered the reaction mass sufficiently fluid for its movement by hydraulic pumps. In recent years this work has been raised to a commercial scale. Using a continuous hydrogen and coal flow two large German industrial units in 1926 are said to have reached an annual output of 1,000,000 barrels of oil.

Since the publication of Bergius work this field has been greatly extended in all directions. Much of this research has been done on oils. Thus Waterman and his associates (26) at the Technical University of Delft have hydrogenated cotton seed oil and paraffin wax. They report efficient conversions to oils with a high gasoline percentage. Most of their work has been done with paraffin since its products are much easier to evaluate than any tar or coal mixture. By comparative experiment they were able to show that hydrogenation has several advantages over the well known cracking still which

is a thermal decomposition process alone. A larger yield of gasoline (63%) and kerosene (19%) was obtained from paraffin. Very little gas and no coke appeared. The liquid reaction products were more saturated than the cracked oils. They also left a smaller residue on distillation.

Waterman believes that the function of the hydrogen in this reaction is to promote a more uniform splitting of the hydrocarbon molecule to give products which do not polymerize to coke. The hydrogen is not used to any great extent in satisfying unsaturated bonds. However this does not agree with the reaction mechanism put forward by other workers in this field. Bergius, for instance, postulates thermal decomposition followed by hydrogen addition at the unsaturated linkages. Kling and Florentin (17) support these views. They believe the unsaturated bodies produced by thermal decomposition are in an activated state. In the presence of an excess of hydrogen, hydrogenation results with the production of short chain hydrocarbons. Otherwise these bodies react with one another, polymerize and form coke as in the cracking reaction. The ideal hydrogenation occurs when the rate of thermal decomposition just equals that of hydrogen addition. And such occurs at a certain definite temperature for each compound. In the case of the complex mixture that exists in a tar or coal various temperatures are necessary for complete hydrogenation.

Originally Bergius did not contemplate the use of catalysts in this work. But an extensive research program by the I.G. Farbenindustrie (18) resulted in a line of catalysts unaffected by the poisoning influence of sulphur.

The I. G. then developed a method for the hydrogenolysis of carbonaceous materials in a continuous manner on a commercial scale. Within the last few years the Standard Oil Co. of New Jersey joined with the I. G. in further development of these methods in the United States, (15). A high pressure plant was located at Baton Rouge, Louisiana. This research station confined itself entirely to the interests of oil refining. Runs lasting as long as 8 months were made on various crude oils without any coke formation. Several advantages over the usual refining methods were claimed. Sulphur was readily eliminated as hydrogen sulphide. Heavy crudes containing a high percentage of asphalt were reduced to low boiling hydrocarbons with a volumetric yield in excess of one hundred per cent. By changing the catalyst and the working conditions they varied the reaction products at will. Thus it was possible to work a particular crude for gasoline, burning oil or paraffinic lubricants. The quality of these products could also be changed. The losses by current refinery practice reach a large figure each year and can be only tolerated so long as crude petroleum is low in cost. Undoubtedly hydrogenation will, in the future, play an important part in the processing of crude petroleum. In place of the wasteful thermal decomposition of the cracking process there is offered an orderly reconstruction of the complex crude to uniform oils.

Considerable research has also been done in England along this line. Dunstan of the Anglo-Persian Oil Company, (5) used ammonium molybdate at 450°C . and 270 atmospheres pressure of hydrogen to obtain yields of 30% of gasoline and

30% of kerosene from a coal tar. Mention should also be made of the work of Shatwell at the Mining Research laboratory at Birmingham University (23). Working with a gas oil at 400°C. and 200 atmospheres of hydrogen he was able to produce substantial yields of low boiling hydrocarbons. Although quite unsaturated these products were of a much higher quality than those obtained by cracking under similar circumstances. He also conducted experiments on a shale oil of high sulphur content and reported a partial desulphurization with the production, as before, of low boiling oils.

Nash and Shatwell also started research on the hydrogenation of British coals (20). They found a solvent necessary for this work and used phenol. Skinner and Graham (25) have continued this work using much the same procedure. In separating the reaction products, precipitation by caustic soda was followed by extraction with chloroform. In this manner the reaction products were separated into a phenol insoluble residue - a phenol soluble, chloroform insoluble brown powder - and a phenol soluble, chloroform soluble tar oil. Graham has continued this work on a large number of coals with less favourable results than those reported by Bergius, (14, 24). The replacement of hydrogen by inert nitrogen gave distinctly unfavourable results.

This work has been criticized because of the use of phenol. Lush (18) in particular, has commented on the experimental use of phenol in this field. Not only is it a product of hydrogenation but he has shown that it is converted to cyclohexane under conditions far milder than in the actual hydrogenation of coal. He has pointed out that the usual

formation of 20% of phenol is cut to 4% when hydrogenation is carried out in the presence of an excess of this substance.

Although this is only a cursory review of the literature of this field it will suffice to indicate the present status of the subject. The literature, largely patents, is characterized throughout by a lack of experimental detail except for a few of the publications of state and university laboratories. As far as commercial development is concerned there are trustworthy reports that large size plants for the treatment of coal and oil operate in Germany. And quite recently, in the United States, crude oils have been refined in commercial quantities by high pressure hydrogenation. A complete review of the whole subject up to the year 1930 has been ably presented by Ellis (8).

PART I.Materials:

Bitumen was obtained through the kindness of Dr. K. A. Clark of the Research Council of Alberta and was prepared from McMurray sands by his separation process. (4). Briefly, in this process, the sand is intimately mixed with sodium silicate solution, heated, and added to a large volume of hot salt water. The bitumen separates and collects on the surface of the water. The properties of the different lots of bitumen supplied did not vary greatly except in regard to water content. Before use, the bitumen was dehydrated by heating at 110-120°C. until the evolution of steam ceased. The chief characteristics of the dehydrated bitumen are as follows:

Carbon,	92.3%	Initial B.P.,	175°C.
Hydrogen,	10.2%	Carbon Residue,	14.2%
Nitrogen,	0.37%	Density, 25°C.,	0.998.
Sulphur,	4.2%		

Commercial electrolytic hydrogen supplied in steel cylinders was used as received. In those experiments referred to later as using methane in place of hydrogen, the source of methane was Viking natural gas. The natural gas was taken from the fuel supply mains and used directly as methane. The gas is dry, sulphur free and contains over 93% methane. The balance is largely nitrogen with small amounts of ethane, propane and 0.1% carbon dioxide.

Different catalytic materials, all ground to pass a

100 mesh screen, were used. For convenience in tabulation in Part I of this paper they are labelled A to F and have the following composition:

- A - Ammonium molybdate.
- B - Ammonium molybdate and iron oxide in equal parts.
- C - Anhydrous aluminium chloride.
- D - Alkalized iron oxide.
- E - Iron, chromium and nickel oxides in equal parts.
- F - Nickel oxide.

No attempt was made to prevent any catalytic effect that the steel autoclave might have on the reactions.

The compression and gas handling equipment consisted of a compressor and gas storage system for operation up to pressures of 5,000 lbs. per sq. inch. Standard types of joints and valves were used (10) in which all seals were metal to metal. The autoclave was designed and tested to withstand 7,500 lbs. per sq. inch at 500°C. The autoclave showed few signs of deterioration and where care was exerted, was absolutely gas tight under the above operating conditions.

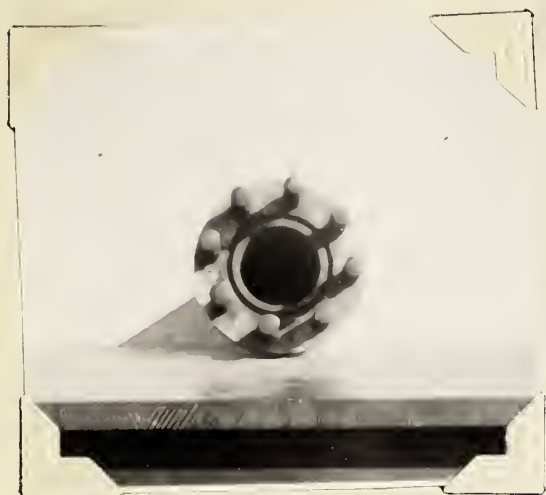
Apparatus:

The flanged autoclave body was machined from solid stock to three inches inside diameter; when fully equipped for operation it had a capacity of 850 c.c. The cover was bolted on by eight stout studs, a tight joint being obtained by the pressure of a tongue in the cover on an annealed copper ring placed in an annular groove in the autoclave body.

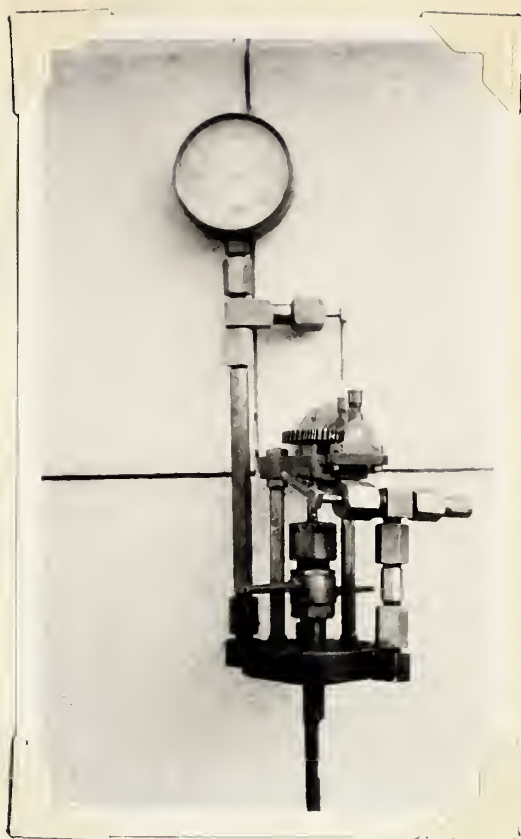
Inlet and outlet valves were provided on the cover which also carried a thermometer pocket, and an anchor type stirrer with its water cooled gland and necessary gearing, which was operated at 40 r.p.m. The autoclave was supported vertically in an electric furnace. It may be pointed out here that this autoclave is not the best for the purpose in hand for a variety of reasons, chief of which are a lack of uniform temperature and poor agitation.

The general appearance of the autoclave is shown by Figure I. A top view of the body is shown in A and a side view of the cover and accessories in B. The inlet and outlet valves, pressure gauge, reducing gear and water cooled packing gland of the stirrer are evident. The assembled autoclave appears in C. and in D it is in position in the electric furnace.

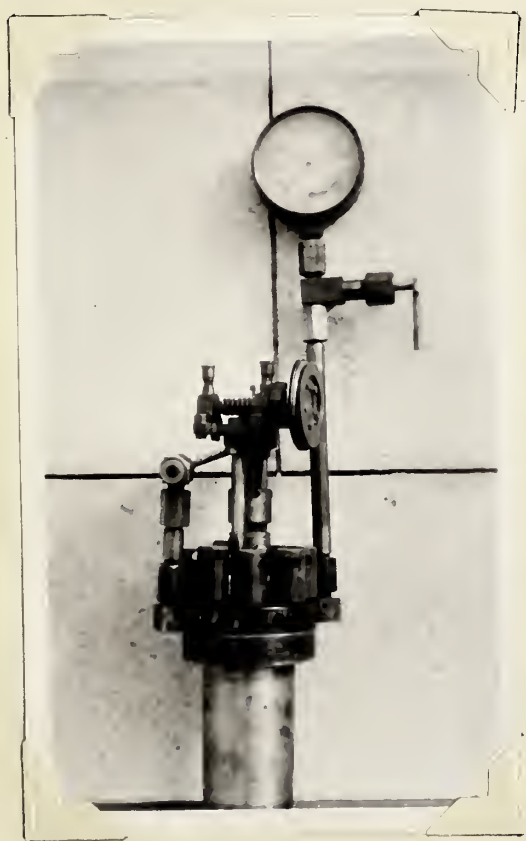
Temperatures were measured by mercury thermometers or by iron-constantan thermocouples connected to a Leeds and Northrup recording controller. They are correct to 3°C. Pressures in pounds per sq. inch were measured on Bourdon tube gauges, calibrated by comparison with a standard test gauge reading to 25 lbs. per sq. inch.



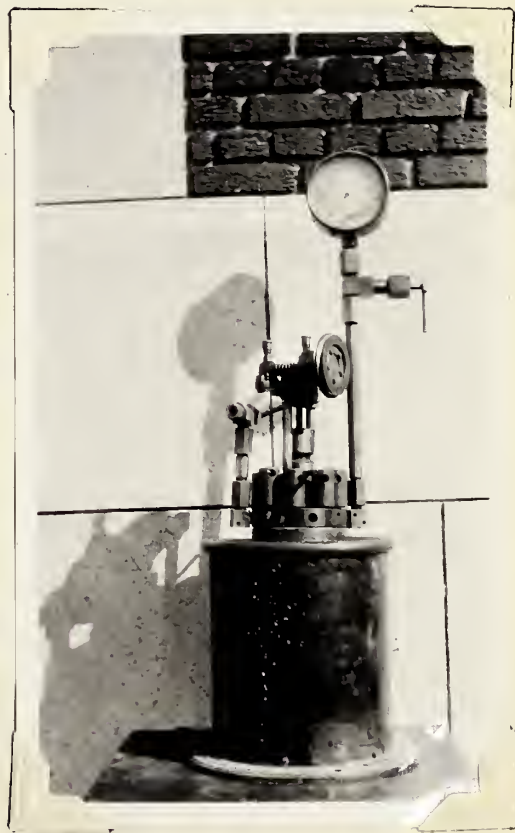
A.



B.



C.



D.

FIG. I.

Procedure:

A sufficient quantity of the catalyst was incorporated with bitumen to give the desired ratio, and a weighed amount, usually between 300 and 400 gm. was placed in the clean autoclave. The autoclave was closed, the connections made, and the air washed out, the pressure being then raised with hydrogen to the initial value. The temperature was raised as rapidly as possible and held to the desired value by hand regulation until steady, when the controller was cut in. Pressures were recorded continuously, or otherwise read and noted at appropriate intervals. Stirring was commenced when the temperature was such that the charge was fluid. Two subsequent procedures were followed. In some instances, after the reaction was complete, the autoclave was cooled and the gas liberated into a gas holder through a test meter. The gas was analyzed after it had reached uniform composition in the gas holder. A further addition of hydrogen could then be made and the process repeated a number of times, or alternatively, the autoclave might be opened after one addition. In other experiments, after absorption appeared complete, more hydrogen was added as often as wanted without allowing the autoclave to cool or removing the residual gas. Finally the autoclave was cooled and the gas measured and collected for analysis. A considerable quantity of the more volatile hydrocarbons passed over with the gas and were collected in a condenser immersed in solid carbon dioxide. They boiled over the range - 40 to + 40°C. and were doubtless largely butane and pentane with some propane. They amounted to 2 to 3% of the original bitumen.

The oil and coke were separated and weighed. No

treatment was used to remove adhering oil from the coke other than allowing the excess oil to drain thoroughly. When possible, the oil was examined for density, viscosity, carbon residue, solubility in sulphuric acid, distillation range and sulphur content. Ultimate analyses and some refining tests have been carried out but are incomplete at present. Densities were determined at 25°C. with a 10 cc. density bottle. Viscosities were found when possible with an Ostwald pipette and are recorded as poises at 25°C. Unsaturation was determined by solubility in sulphuric acid according to the method of the United States Bureau of Mines with centrifugal separation. Carbon residue was determined with Conradson's apparatus and the distillation range was found by the A. S. T. M. kerosene distillation apparatus.

For a number of reasons, sulphur was not determined by any of the common methods. Accuracy and, because of the large number of determinations, speed, were desired. The lamp method was useless on the oils produced from bitumen because of suspended colloidal carbon and mineral matter. The oxygen bomb is accurate but tedious and time consuming. The Escha and sodium peroxide methods are inaccurate unless a great deal of time and care are taken. Other work on the determination of total sulphur in gases led to a satisfactory method. Weighed oil samples, held in sulphur-free siliceous earth, were placed in a quartz tube heated electrically as customary in organic combustion analysis. The tube was packed with platinum and kept at 900°C., except in the region of the oil sample. Provision was made to raise the temperature of the oil slowly to 900°C. and at the same time to have a brisk

stream of air passing through the tube. The oil was volatilized and burnt completely; the products of combustion in the air stream were washed by standard sodium carbonate solution and the quantity of sulphur dioxide determined by titration with standard hydrochloric acid. The method was tested with pure sulphanilic acid and found satisfactory even in the presence of so much combined nitrogen. Blank test runs showed that no correction was necessary. A determination required 1.5 to 2 hr. and the method is applicable to solids or liquids even as volatile as benzene. Duplicates agree to better than 0.01%, using one-gram samples of oil containing 2% sulphur. If such accuracy is not desired, considerable time can be saved by increasing the air flow and using smaller samples.

Results and Discussion:

The chief experimental details of the more successful experiments are given in Table I. This work may be divided into two parts. Experiments 23 - 47 indicate the effect of H_2 under high pressures on the bitumen at temperatures ranging from 340 to 400°C. in the presence and absence of catalysts. In experiments 10, 46 & 48 the tar was heated under high methane pressures with Al_2Cl_3 as a catalyst. A cracking experiment - 49 - under the thermal pressure of the bitumen at 400°C. was also run for purposes of comparison.

It is evident that there is a considerable discrepancy in material balance in many of the cases given in Table I. This loss may be due to several causes: first, leaks in the autoclave joint at high temperatures; second, loss of volatile constituents in the exit gas as vapour and foam; and lastly, loss of oil by evaporation while recovering the products of the reaction. A small amount of coke was also lost due to its adherence to the autoclave walls. It is to be noted that the more serious of these losses would tend to decrease the oil yield only. Recorded oil recoveries are as a result low in all cases. In experiments 34 & 40 obvious leaks and consequently high percentage losses prevented the calculation of gas yields and hydrogen absorption. Losses are also rather high in experiments 23, 32, 33 and 46. However, calculations are included for these.

Experiment 35 was run on a sample of the natural tar sands, containing 15% of bitumen. Three additions of hydrogen were made at 400°C. After reaction, however, it was impossible to separate the oil and sand. It is worthy of note that a

TABLE I.

HYDROGENATION OF BITUMEN - COOK AUTOCLAVE.

Experiment no.	23	25	26	29	30	31	32	34	35	36	37	38	39	40	46 ¹	47
Wt. charge in gms.	335	267	355	350	360	365	384	415	460	201	356	383	340	350	360	340
Catalyst, %	nil	nil	1.4A	1.3A	2.7B	1.4A	0.4A	0.4A	0.4A	0.5A	1.6C	nil	0.6D	0.6E	0.9C	5.6F
No. of cycles	2	1	4	4	6	7	5	7	3	3	6	3	2	2	2	2
Time/cycle in hrs.	3	5	2	4.5	5	1	1.5	3.5	2	4	5	3	4.5	6	4	4
Ave. temp. °C.	340	380	360	360	380	380	380	400	400	400	400	400	400	400	350	400
Initial Pressure, lbs. per sq. in.	710	1175	1175	1175	1175	1175	1192	1175	1443	1165	1080	1220	1160	1360	950	1250
Maximum Pressure	1175	2470	1865	1830	2930	3370	3700	3360	1863	3090	2360	2970	2690	2500	2100	2400
Final Pressure	595	786	474	530	-	-	618	575	1013	-	-	900	-	600	850	700
Pressure drop	115	389	701	645	-	-	574	600	430	-	-	320	-	760	100	550
Hydrogen absorbed, %	0.4	0.7	1.2	1.0	2.2	3.0	2.3	-	0.9	1.9	2.8	1.5	1.2	-	-	1.3
Gas yield (litres)	8.5	66.0	26.3	33.0	53.7	120.0	55.3	-	29.2	180.0	133.0	69.3	85.0	-	83.9	96.5
Oil %	89.6	73.8	73.4	92.8	85.9	68.0	73.4	69.6	-	55.0	71.5	74.5	72.5	64.3	62.0	73.5
Coke %	0.0	23.6	21.1	0	10.0	18.0	10.8	3.6	-	42.4	11.4	10.5	19.1	14.3	20.9	17.1
Gas %	0.6	-	-	2.8	5.6	9.3	3.8	-	2.6	17.5	9.0	5.6	6.5	-	6.2	5.7
Loss %	9.8	2.6	5.5	4.3	0.0	4.7	12.0	19.5	-	0.0	8.1	9.4	1.9	18.9	10.9	3.7
% bitumen to gasoline	7.7	32.5	19.8	7.4	31.7	34.6	27.9	32.7	-	30.8	34.4	29.0	30.4	25.7	11.8	30.8
% bitumen to oil, below 300° C.	24.2	45.8	33.0	18.6	49.7	47.6	40.4	45.2	-	38.5	50.7	44.7	43.5	40.0	21.7	47.8
Gas % -																
CO ₂	1.2	nil	1.3	10.6	4.0	1.4	2.0	1.6	0.4	1.4	0.7	2.2	4.4	4.8	3.1	2.7
CnH _{2n}	0.6	16.8	5.1	3.6	14.6	1.7	1.5	8.0	6.0	7.1	7.2	1.5	1.9	3.4	1.3	1.4
H ₂	82.6	2.4	5.1	40.6	2.3	53.5	40.5	39.9	74.3	61.4	73.1	34.4	36.9	34.8	3.1	48.1
C ₂ H ₆	nil	71.5	77.4	33.2	-	-	17.0	10.0	4.4	6.9	2.5	23.3	24.5	32.5	14.0	18.5
CH ₄	13.0	5.9	19.0	13.2	-	-	33.0	32.7	12.5	20.5	13.0	44.0	32.5	20.8	75.1	14.4
Oil - Density at 25°C.	0.993	0.920	0.926	0.969	0.914	0.874	0.904	0.890	-	0.852	0.878	0.887	0.891	.915	.922	.898
Viscosity at 25°C.	-	0.052	0.160	-	0.033	0.025	0.050	0.022	-	0.012	0.026	0.033	0.030	0.042	-	0.029
C. Residue %	14.1	7.5	6.7	11.3	5.6	3.4	5.6	4.4	-	2.5	4.3	5.6	6.4	8.5	8.3	6.2
Unsaturation %	-	49	48	-	45	20	36	23	-	34	32	39	38	64	39	52
Sulphur %	-	2.46	-	-	2.24	-	-	-	-	-	1.40	2.36	2.60	-	-	2.09
Initial B.P. °C.	105	48	60	110	60	42	41	38	-	36	35	40	37	45	50	43
% at 200°C.	8	38	22	8	30	45	31	40	-	45	40	33	38	34	15	35
% at 300°C.	27	62	45	20	58	70	55	65	-	70	68	60	62	62	35	65
End point	319	341	348	319	331	355	342	363	-	359	354	353	338	341	352	325
Pitch	32	18	20	30	24	16	20	20	-	22	20	20	26	25	18	27
M.P. of pitch °C.	-	-	-	130	55	53	100	80	-	-	52	75	37	71	-	-
C-H ratio	1.49	1.45	1.47	1.50	1.47	1.46	1.44	1.56	-	1.59	1.68	1.65	1.66	1.66	-	1.75

1. - Initial pressure; 950 lbs. of Viking gas.
2. - Initial pressure; 900 lbs. of Viking gas.
3. - Initial pressure; 15 lbs. of Viking gas.

46 ¹	47	48 ²	49 ³	10
360	340	370	340	385
0.90	5.6 ^F	5.4 ^C	nil	11.7 ^C
2	2	2	1	1
4	4	4	6	5.5
350	400	350	400	360
950	1250	900	14.7	978
2100	2400	2250	1600	4190
850	700	800	500	1110
100	550	100	-500	-132
-	1.3	-	-	-
83.9	96.5	-	103.0	155.0
62.0	73.5	58.8	50.7	56.0
20.9	17.1	26.5	35.3	36.8
6.2	5.7	11.4	8.1	11.1
10.9	3.7	3.3	5.9	5.9
11.8	30.8	11.8	24.4	26.3
21.7	47.8	22.4	33.9	31.9
3.1	2.7	3.1	5.4	0.5
1.3	1.4	1.3	1.4	2.3
3.1	48.1	4.3	11.3	0.6
14.0	18.5	15.5	28.1	94.2
75.1	14.4	71.6	52.2	nil
..922	.898	.934	.886	-
-	0.029	-	0.022	-
8.3	6.2	7.9	6.6	0.9
39	52	44	38	-
-	2.09	-	-	-
50	43	58	41	30
15	35	17	42	42
35	65	38	67	57
352	325	333	334	260
18	27	46	25	43
-	-	-	-	-
-	1.75	-	-	-

.9% absorption of hydrogen occurred.

In the case of the methane experiments the resulting increase of the final cold pressure over the pressure of methane added, is recorded as a negative pressure drop. It may be that the pressure drops given for experiments 46 & 48 are due to loss of gas while at temperature.

The crude autoclave oils are all of a dark black or brown colour, because of suspended carbon. Much of this carbon is lost by settling. The A. S. T. M. distillate was originally a straw yellow in colour but the deposition of gums changed this colour to a dark brown. The sulphur content of the distillate below 300°C. is about half that of the original bitumen. The remainder appears as hydrogen sulfide in the exit gas. No attempt was made to determine the proportions of this in the recovered gases. The unsaturation value is high but does not represent the true unsaturation compounds so much as those hydrocarbons and tar acids soluble in sulphuric acid. Preliminary refining experiments involved a sulphuric acid wash in the ratio of one part of acid to thirty parts of oil, a dilute alkalic wash and distillation. The washing process produced a straw yellow oil of good odour having a water-white gasoline distillate which did not deteriorate on standing. The residue showed a slight darkening in colour, but no decomposition to carbon. Quantitative data are lacking in such small scale experiments but the quantity of sludge from the washing process did not appear excessive.

It might be remarked that the recorded gas analysis values are averaged, consideration being taken of the volume

of the gas recovered in each cycle of an experiment.

The effect of an increasing temperature is shown in experiments 23, 25 and 38 which were run in the absence of a catalyst. The percentage of hydrogen absorbed increases directly with temperature; coke formation, negligible at 340°C., reached considerable proportions at the higher temperatures. Gas formation is considerably higher at 380°C. and reaches a maximum at 400°C. The pressure drop on the other hand is greater at 380°C. than at 400°C. At the latter temperature cracking undoubtedly produced large volumes of gaseous hydrocarbons. Thus the amount of bitumen gasified reaches a value of 29% at 400°C. Conversion to gasoline and kerosene also proved to be higher at 380°C., reaching a combined percentage of 46%. The optimum temperature of reaction without a catalyst would appear to be in the neighborhood of 380°C. since cracking is predominant at higher temperatures. This is considerably below the value of 450°C. usually used in the hydrogenation of coal and coal tar, (14). Considerable doubt exists however in regards the stirring efficiency and constant temperature control of this type of autoclave. Overheating undoubtedly occurred, so that the recorded temperature seldom represented the true state of affairs.

At 380°C. experiments 30 and 31 bring out the advisability of using catalysts in this work. The percentage weight of hydrogen absorbed is increased to 2.2 and 3.0% as compared to 0.7% at the same temperature in the absence of a catalyst. Conversion to gasoline and kerosene reaches a value of 50% which represents a 4% increase over experiment 25. On the average the coke production is also lower for these

experiments. However, these conclusions do not apply to all of the catalysts used. The best catalysts are ammonium molybdate and aluminium chloride. Surprising as it seems aluminium chloride has a favourable action in producing little gas and coke. It has the disadvantage of being corrosive and yielding an oil containing hydrogen chloride. The other catalysts are all definitely less active but as far as can be determined have a beneficial effect. From the apparent rate of reaction it might seem that the addition of a catalyst is hardly worth while. The time saved is small. However, the catalyst is very useful from the point of view of coke and gas production. These are invariably smaller when a catalyst is present, due no doubt to the greater rate of hydrogen absorption as compared to cracking in the initial stages of the reaction. The catalyst is probably largely removed ultimately by combination with sulphur. The over all rate of reaction is not much improved by its presence. The catalysts have a further important advantage in permitting a lower working temperature. Not only do they prevent cracking to some extent but catalysts also minimize wear and tear on the apparatus.

From the amounts of coke obtained in experiments above 360°C. it is evident that cracking competes successfully with hydrogenation in the reaction chamber. This is undoubtedly a fault of the autoclave design. Uneven heating is responsible for the trouble. The lower part of the autoclave was very much hotter than the upper part. Moreover, the action of the stirrer was in general poor and did not prevent the building up of coke on the autoclave walls which

would lead to superheating. The surface of bitumen exposed to hydrogen was small because of the shape of the autoclave. Since cracking depends on a low hydrogen concentration and on a high temperature the result is such a reaction in these lower portions of the autoclave mixture. The reaction is exothermic and spreads fairly rapidly throughout the reaction mixture. Large amounts of coke are necessarily formed.

The rate of hydrogen absorption is most important and it is readily indicated by the variation of pressure with time. In Figure II as typical examples are plotted, the results of experiments 25, 26 and 38.

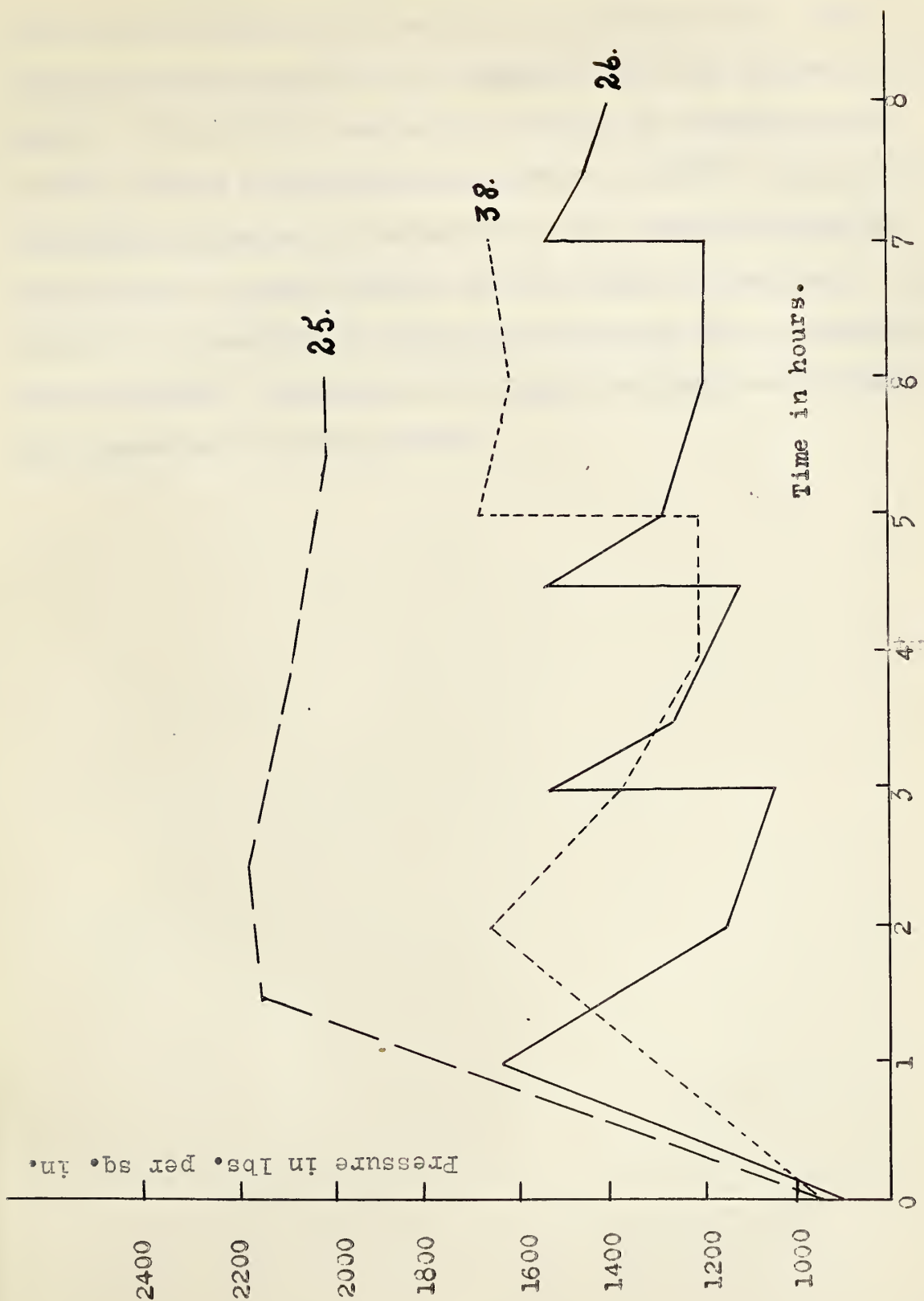


Fig. 2 Pressure-Time chart of expts. 25, 26 & 38.

Four additions of hydrogen were made in experiment 26, one in experiment 25 and two in experiment 38. The effects of temperature and a catalyst are made evident in these curves. No catalyst was used in either of experiments 25 or 38, and the temperatures were 380 and 400°C. The rate of hydrogen absorption as indicated by the downward trend of these curves is much greater at the higher temperature. The effect of a catalyst is shown in experiment 26 at a temperature of 360°C. In spite of the lower temperature the rate of hydrogenation is much greater.

The effect of temperature is also important and pressure readings do not give complete information. Below 360°C . the reaction is very slow. The pressure remains practically constant even though hydrogen is being absorbed as shown by subsequent gas analysis. Apparently the rate of hydrogen absorption just equals the rate at which gaseous hydrocarbons are produced by cracking. At 400°C . both reactions are considerably more rapid and the pressure comes finally to a constant value. Experiment 39. demonstrates this case. The pressure reached a constant maximum value of 1,890 lbs. per sq. inch and the hydrogen concentration dropped to 45%. A further addition of hydrogen produced a constant pressure of 2,600 lbs. and a final hydrogen concentration of 48%. In many instances, on the other hand, an initial pressure drop is followed shortly by a steady increase due to the formation of methane and other gaseous hydrocarbons. The last half of experiment 38 is typical of this behaviour.

Figure II clearly indicates that the absorption of hydrogen apparently ceases when the pressure has dropped to two-thirds of its maximum value. The partial pressure of hydrogen for this point is much lower being in general $1/5$ or $1/6$ of the maximum pressure or one-half of the final cold pressure. It is also probable that after the cessation of hydrogen absorption the cracking reaction goes to completion. The behaviour of experiment 38 is along these lines. In the absence of a catalyst the pressure of hydrogen at which absorption ceases is higher. Cracking, then, starts much sooner. For equal lengths of time coke production would be higher where no catalyst was used.

From the practical point of view the time of reaction is important. The curves show that the bulk of reaction occurs in the first two hours and a good deal of that in one hour. Generally however, three to four hours were allowed for absorption. In producing oil in commercial quantities the hydrogen pressure would necessarily be maintained at maximum pressures to obtain the most rapid reaction. The greatest utilization of hydrogen would be obtained by the use of a counter current system of gas and bitumen flow in a series of autoclaves.

A comparison of hydrogenation with cracking experiments is of interest in showing the difference in oil and coke production. In experiment 49 bitumen with no catalyst or gas was heated to 400°C . for six hours in the closed autoclave. The maximum pressure was 1,600 lbs. per sq. inch and the final cold pressure 500 lbs. per sq. inch. The experiment yielded 103 litres of gas per kilogram of bitumen, 35% of coke and 50% of oil. The latter figure represents a 34% conversion of the tar to unrefined gasoline and kerosene. The corresponding figure for hydrogenation is about 50%. The oil obtained was of a good grade: density 0.836, viscosity 0.022, 38% unsaturated, I.B.P. 41°C . Egloff and Morrell have applied the Dubb's cracking process to this bitumen at a pressure of 90 lbs. per sq. inch (6). The pressure distillate was 56% while 42% coke and 1.7% water were formed. They estimate that 45 - 50% of the bitumen may be converted to N.E.P. gasoline of high anti-knock value by successive cracking of the resulting oils. From the yields of experiment 49 it is seen that such a technique would produce similar results in this work.

A comparison of these hydrogenation and cracking experiments shows clearly that the process of hydrogenation is superior to cracking in virtue of larger oil yields and smaller coke production. Gasoline yields cannot as yet be strictly compared by the A.S.T.M. tests recorded. The oil yields were not of a sufficient size to allow the collection of quantitative refining data.

A series of experiments on cracking under high pressures of natural gas in the presence of aluminium chloride as a catalyst showed a great reduction in coke and gas production with a consequent increase in oil yield as compared to cracking in experiment 49. Coke production averages about 25% for experiments 10, 46 and 48. Approximately 11% of the bitumen is gasified in each case. In experiment 10, conducted at 360°C. the conversion to gasoline was 26% as compared to 24% at 400°C. at lower pressures in the absence of a catalyst. The kerosene yield varied in the same proportions. In spite of the lower temperature more oil has been produced. However, the improvement in yield is so slight that further work along the lines of high pressure cracking is hardly warranted.

Summary:

In these preliminary experiments bitumen from the tar sands of Fort McMurray was hydrogenated to form a light crude oil, amounting in some cases to 80% of the original bitumen. This was easily refined and produced a water-white stable gasoline representing a bitumen conversion of as high as 35%. It was apparent that these results, obtained under unsatisfactory conditions, could be surpassed in more appropriate apparatus.

The optimum temperature was in the neighborhood of 380°C. but considerable doubt attaches to this value because of overheating effects and inefficient stirring of the charge.

The best catalysts used were ammonium molybdate and aluminium chloride. However, use of the latter resulted in definite amounts of hydrogen chloride in the gas and oils produced by the reaction.

Under favourable conditions an absorption of hydrogen equivalent to 3% by weight of the bitumen was attained.

The oil had a sulphur content equal to about one-half that of the bitumen; the difference probably appearing as hydrogen sulphide in the recovered gases and being recorded as carbon dioxide.

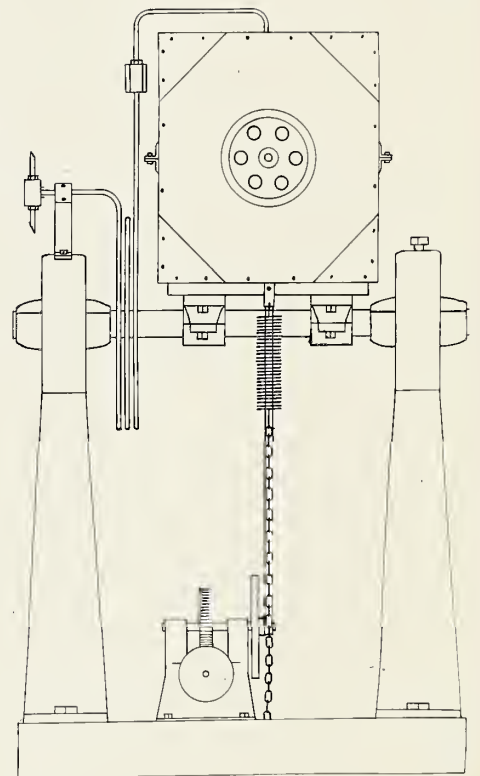
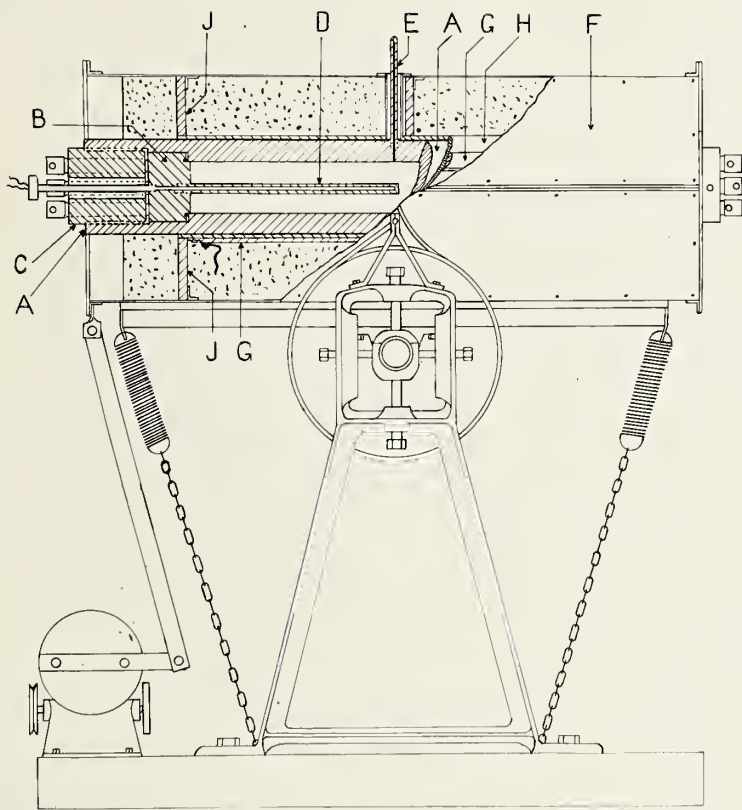
PART II.Materials:

In this second series of experiments the raw materials are identical with those described in Part I. Only three catalysts were employed however, two of which have been mentioned previously; ammonium molybdate and aluminium chloride. A new catalyst, molybdic anhydride, was used to the greatest extent in this series. It appears to be as efficient as the ammonium salt and has the advantage of not adding ammonia to the system. The anhydride was prepared by ignition of ammonium molybdate. Ammonium molybdate was used in only a few experiments and aluminium chloride only once on a very resistant residual pitch.

Apparatus:

The compression and gas storage system were essentially as described before. The capacity has been greatly increased and the methods of manipulation of the compressed gases improved in many respects. Pressure measurements were almost always recorded continuously on a Bourdon tube recording gauge, calibrated at intervals by comparison with a standard test gauge. Temperature measurements were made as before with calibrated iron-constantan thermocouples and a Leeds and Northrup recording potentiometer controller. This instrument enabled temperature control to $\pm 5^{\circ}\text{C}$.

The autoclave and its supporting apparatus that permitted agitation by oscillation of the furnace and autoclave is shown schematically in Fig. III. The arrangement is similar to that described by Peters and Stanger (21). The autoclave shell, A, was machined from KA₂ nickel chromium steel and designed for service to 7,500 lbs. per sq. inch at 500°C. The shell was in the form of a tube and was closed at each end by a standard method (10) employing six bolts in compression bearing on end plates, B, seated on a confined ring of soft copper. It was found advisable to protect these copper rings from the action of sulphur by inner aluminium rings of smaller diameter.



Aluminium was not satisfactory alone at the high temperatures used.

The stress was transmitted from the end plates^s to the shell through a ring nut, C. which was screwed into the shell by buttress threads. The ring nut and compression bolts were found satisfactory when made of chrome-vanadium steel. The end plates, B, were drilled and threaded in the centre of the outside faces, thus allowing the use of a draw bar to assist in their removal. One end plate carried a thermocouple well, D, which extended co-axially inside the shell to its centre. A gas connection, E, was made to the reaction chamber at its mid point as shown. The capacity of the autoclave was 1,800 c.cm. when assembled. The machine was readily opened by loosening the compression bolts about half a turn and then screwing out the ring nut.

The autoclave was supported in a split electric furnace, F, heated by five 500 watt strip heaters, G. These were spaced uniformly about the autoclave so that three were in the lower half of the furnace and two in the upper half. The furnace casing of sheet metal on a light angle iron frame carried the weight of the insulation only. A split pipe, H, carrying the heaters, was bolted to steel cross members, J, which were supported by the base plate of the furnace. Both halves of the furnace were fitted in the same manner and the upper half bolted to the lower along an outside longitudinal flange. The autoclave fitted snugly within the two halves of the split pipe and rotation was prevented by two lugs which fitted recesses in the pipe. The use of a metallic casing, in this case $\frac{1}{4}$ in. thick, through

which the heat was transmitted to the autoclave, assisted in producing and maintaining a uniform temperature. The furnace was readily dismantled and the autoclave removed for examination when necessary. The installation of new strip heaters was accomplished by taking out the split pipe to which the heaters were bolted.

The base of the furnace was attached to two flat boxes fitted on a shaft which was supported at each end by inverted shaft hangers. An oscillating motion was imparted to the furnace and contained autoclave by a motor driven reducing gear operating a crank and connecting rod mechanism. The crank throw was 6 in. and 20 complete oscillations per minute were made. To ensure smooth operation of the mechanism springs were stretched from each end of the furnace base to chains of adjustable length attached to the floor. The spring tension was regulated to take most of the weight of the apparatus as it departed from the horizontal position.

Gas connection was made to the inlet, E, through a flexible copper coil of three turns, 12 inches in diameter, which was centred on the bearing shaft. The outer end of this coil was terminated by a T connection, one branch leading to the pressure gauge, the other to a high pressure oil trap. From the oil trap the gas line was led to the gas compression system, and a second line was led to the expansion valve. The outlet of the expansion valve was connected to an oil filled wet test gas meter and a gas holder. Heat control of the autoclave was accomplished by adjusting the voltage on all or any of the strip heaters at from 110

to 220 volts. A magnetic switch was operated by the potentiometer controller and produced the desired changes in voltage in accordance with the temperature variation.

Procedure:

The experimental procedure was similar in most respects to that described above in Part I. The quantities of bitumen were varied from 375 to 1,200 gr. The charge of bitumen was added to the clean autoclave through one end and after closure was effected the apparatus was flushed with hydrogen. When a catalyst was employed, the powdered material was thoroughly incorporated into the bitumen before the charge was placed in the autoclave. No liners of any sort were used in the reaction vessel and no corrosion of the steel has occurred to date. Any catalytic effect of the steel was present in all experiments.

About two to three hours were required to heat the autoclave to reaction temperatures. Oscillation was commenced at 150°C. at which temperature the charge was fluid and reaction negligible. The temperature was maintained at a constant value until the pressure ceased to drop and on occasion had passed through a minimum and rising pressure gave evidence of cracking. The time to the minimum pressure varied from four to less than one hour as the temperature of the experiment was changed from 380 to 450°C. After cooling overnight, the gas was released at the expansion valve to the gas meter and thence to the gas holder, from which samples were later removed for analysis. Hydrogen sulphide was determined by allowing a definite volume of the gas to bubble through a standard iodine solution in a Meyer absorption tube inserted between the expansion valve and the gas meter. On occasion condensers were inserted in

the same place with the object of collecting the volatile hydrocarbons in the gas. Usually these hydrocarbons were removed by absorption in the oil of the gas meter. They amounted to from 1.5 to 2.0% of the original bitumen and boiled below 40°C.

This general procedure was repeated from one to four times in different experiments, before opening the autoclave. Each repetition, hereinafter, will be termed a cycle. The product in the autoclave was removed and was bottled as rapidly as possible. However, losses always occurred due to the evaporation of volatile hydrocarbons and a certain amount of foaming in some cases. Moreover, a loss was occasioned by the film of oil remaining in the autoclave. Coke was determined by filtering the reaction product and allowing the adhering oil to drain for some time. Because of the incomplete removal of the oil by this process recorded coke yields are in general higher than is actually true. The oil yield was consequently lower than the true value on this account, in addition to those losses mentioned above. The hydrogen absorption was calculated from the difference between the quantity of hydrogen added to the cold autoclave and that recovered in the gas holder as given by the meter readings and gas analysis. This value is expressed in per cent. by weight of the original bitumen.

The methods of oil analysis are described in detail in Part I of this paper. In this work they were supplemented frequently by determinations of carbon and hydrogen and occasionally by nitrogen determinations. Nitrogen was determined by a modified Kjeldahl method (22) but sufficient

data have not been obtained to indicate the fate of the nitrogen in the bitumen on hydrogenation. The few analyses that have been carried out show that the nitrogen content of the oils is about one-half that of the bitumen. Gasoline, kerosene and gas oil were determined by distillation through an 18 in. fractionating column. In a few experiments the lubricating oil and paraffin were obtained by vacuum distillation to 300°C. in the same column.

Results and Discussion:

The details of individual experiments are presented in what follows as groups tabled together because of their value as comparative data. In some instances the course of individual experiments is illustrated by figures showing the changes of pressure with time and temperature.

The tables are in general self-explanatory, although some remarks may be appropriate in regards to certain values. Each addition of hydrogen, heating, cooling and removal of gas, is termed a cycle and each experiment on a sample of bitumen includes one or more of such cycles. The row headed average time per cycle refers to the time during which the autoclave was within 5°C. of the temperature of the experiment. This time does not give the total reaction time since hydrogenation commenced at some temperature below 350°C. The gas analyses represent the mean of the gas analyses for each cycle, account being taken of the different volumes of gas recovered in each cycle. Viscosity values are given in poises and were determined in an Ostwald pipette. The unsaturation value for the crude oil gives its solubility in 98% sulphuric acid and includes olefines, aromatics and unaltered bitumen. The data for crude and refined gasoline were determined on the whole of the crude oil except the small fraction required for the other tests. Occasionally the gasoline yield was calculated from the A. S. T. M. distillation. Refining methods consisted in washing the crude gasoline in turn with 10% alkali, 80% sulphuric acid, 10% alkali and water. No attempt was made to remove sulphur which amounted to less than 0.5 per cent. in the gasoline. A stable water-white gasoline was produced by the above process.

In regards to the yields of gas and coke, it is necessary to emphasize that the coke figures are high and that the oil figures are low compared to the true yields. Oil remaining in the coke and evaporative losses both lower the yield found. A removal loss of from 5 to 10 per cent. may be attributed to the oil fraction in experiments using 1,200 to 700 gr. charges. In those experiments using smaller charges the mechanical losses are proportionally higher. Other sources of loss sometimes occurred, due to leaks in the autoclave closures and excessive foaming of the product. Such experiments are all in the series using large charges and are obvious in that the loss tabled is greater than 10%. No leaks and no foaming occurred in any of the experiments with the smaller charges.

1. Hydrogenation of Bitumen at 380°C. to 400°C.

The pertinent data of a number of experiments on 1200 gr. charges of bitumen at 380°C. to 400°C. are presented in Table II.

Molybdic anhydride was added to the extent of 0.5 per cent. in all experiments but one.

The yield of light oil boiling below 350°C., varied from 40% to 60% as the temperature was raised from 380°C. to 400°C. This increase in oil production is evident from an inspection of the A.S.T.M. distillation data. The crude and refined gasoline yields follow the temperature in the same manner. The other properties such as density, viscosity, etc., parallel the temperature and can be used as guides to the results of hydrogenation.

TABLE I I

HYDROGENATION OF BITUMEN IN 1200 GR. CHARGES AT 380°C. TO 400°C. IN THE
PRESENCE OF MoO₃.

Experiment number	58	59	60	61	64
MoO ₃ %	0.5	0.5	0.5	0.5	0.0
Number of cycles	3	3	5	4	4
Time, hours per cycle	3.0	3.3	3.6	2.5	2.5
Average temperature, °C.	400	390	380	390	400
Average initial pressure, lbs. per sq. in. (cold)	1635	1570	1450	1385	1105
Average maximum pressure lbs. per sq. in. (hot)	3435	2925	2910	2920	2365
Average final pressure, lbs. per sq. in. (cold)	640	505	620	645	445
Pressure drop per cycle, lbs. per sq. in. (cold)	995	1065	830	740	660
Hydrogen absorbed, % by wt. of bitumen	1.1	1.1	1.3	1.1	1.0
Gas yield, less H ₂ , litres per Kg. bitumen	33.2	40.2	36.4	40.4	57.2
Bitumen to oil, %	81.8	81.1	91.4	90.5	71.3
Bitumen to coke, %	5.2	7.2	0.0	0.0	7.2
Bitumen to gas, %	1.7	2.0	1.8	1.6	3.0
Loss %-	11.3	9.6	6.8	7.9	18.5
Bitumen to gasoline, %	26.1	16.6	13.8	17.0	23.0
Refined gasoline, %	18.1	13.5	11.6	13.1	19.6
Gas Analysis, %					
CO ₂	5.5	14.0	7.7	6.7	8.3
CnH _{2n}	1.6	2.6	1.7	1.9	1.7
H ₂	34.3	31.3	56.4	51.4	24.3
C ₂ H ₆	18.0	22.8	11.6	17.8	23.6
CH ₄	28.6	18.1	10.1	14.3	31.0
H ₂ S	3.3	3.8	2.0	4.5	3.9
Oil Properties,					
Density, 25°C.	0.920	0.934	0.922	0.933	0.920
Viscosity, 25°C.	0.097	0.241	0.266	0.332	0.081
Carbon Residue, %	8.1	10.0	7.2	9.0	12.5
Unsaturation, %	51	50	56	49	50
Sulphur, %	1.66	1.61	1.42	1.56	1.43
Initial B. P. °C.	61	57	58	65	76
Per cent. at 200°C.	24	17	17	17	24
Per cent. at 300°C.	49	43	38	35	48
End Point, °C.	326	313	310	318	361
C:H ratio	1.76	1.80	1.82	1.81	1.82
Per cent. Pitch	40	50	59	59	36

Comparing experiments no. 58 and no. 64 it will be seen that the catalyst has little effect on the properties of the oils. The sulphur content of these oils is less than half that of the bitumen, the difference appearing in the gas phase. The carbon dioxide appearing in the gas is somewhat high even when account is taken of the hydrogen sulphide which is included in these values. No explanation of this is forthcoming other than to attribute the carbon dioxide to the thermal decomposition of carboxylic acids in the bitumen. Water is not formed in visible amounts and this lends support to the idea of decomposition rather than hydrogenation of the acids. The coke and gas production do not allow of any conclusions. It might be pointed out, though, that the gas production is much larger in the absence of a catalyst.

Vacuum distillation after gasoline removal of the 400°C. oils yielded a kerosene and lubricating oil fraction amounting to 27% of the original bitumen. Refining of this distillate produced a straw yellow, stable oil which was redistilled to yield 25% of its volume as lubricating oils.

As an indication of the chemical nature of the oils produced, an analysis by the method of Egloff and Morrell (7) was carried out on the combined gasoline fractions. The method yielded the following results:

Unsaturated hydrocarbons	11.7%
Aromatic hydrocarbons	2.3%
Naphthenes	16.2%
Paraffins	69.8%

Presumably the crude oil as a whole would show larger relative percentages of the naphthenes and paraffins.

Analysis of the crude oil showed it to contain 15 per cent.

of bitumen.

It will be noticed in Table II that the hydrogen: carbon ratios are given as atoms of hydrogen per atom of carbon. The values were obtained with the A.S.T.M. distillate and vary only slightly from oil to oil. This slight variation is typical of all ultimate analyses on crude oils and various fractions of the crude oils. Appreciable variation does not appear among the different oils of corresponding fractions. Table III shows the result of an analysis carried out on the oils of experiment no. 61 and may be taken as representative of all the oils.

TABLE III
Ultimate analysis of oils from exp.61.

	Bitumen	Crude Oil	A.S.T.M.			Vacuum fraction to 250°C. less Gasoline
			Distillate	Pitch	Gasoline	
Carbon	82.3	84.9	85.0	86.4	84.6	86.2
Hydrogen	10.2	11.8	12.7	8.7	14.2	11.6
Sulphur	4.2	2.4	1.4	-	0.5	-

Complete reduction of bitumen to gasoline involves the absorption of slightly more than 4% by weight of hydrogen. Less than half this figure appeared to be the maximum absorption in any one static experiment. It will be shown later that hydrogenation of the oil residues from distillation leads to a total absorption of over 3 per cent. in some cases.

The crude oil shows an increase of 1.6 per cent. in hydrogen content over the bitumen and the hydrogen: carbon

ratio is correspondingly higher. A discrepancy is apparent between the analysis of the crude oil and the weighted mean of the analyses on the A.S.T.M. distillate and pitch. This is due to a loss of volatile hydrocarbons in the distillation. The small coke formation in experiment no. 61 taken with the change in hydrogen content of the bitumen after its conversion to oil, shows without doubt that hydrogenation has occurred.

In Figs. IV and V are plotted the pressure-time and pressure-temperature curves of experiments no. 58 and no. 64 respectively. They are quite similar to the corresponding curves of other experiments and are included as examples to emphasize general conclusions. These curves are of interest inasmuch as they give considerable information as to the course of the reaction in individual cycles. They also permit of some speculation as to the process of hydrogenation. The pressure-time curves give information in regards to the rate of hydrogen absorption and show clearly the point at which cracking predominates. The pressure-temperature curves represent a combination of the vapour pressure curve of the bitumen and the effect of temperature on the pressure of hydrogen at constant volume. In the absence of an hydrogenating reaction, the slope of this curve should increase with temperature. Presumably, therefore, the point where this slope becomes constant or begins to decrease in value will indicate the initial stages of hydrogenation. This point, which is the beginning of the inflection of the pressure curve, defines the commencement of hydrogenation with some degree of precision. Other methods of plotting that are commonly used for vapour pressures are of little value in

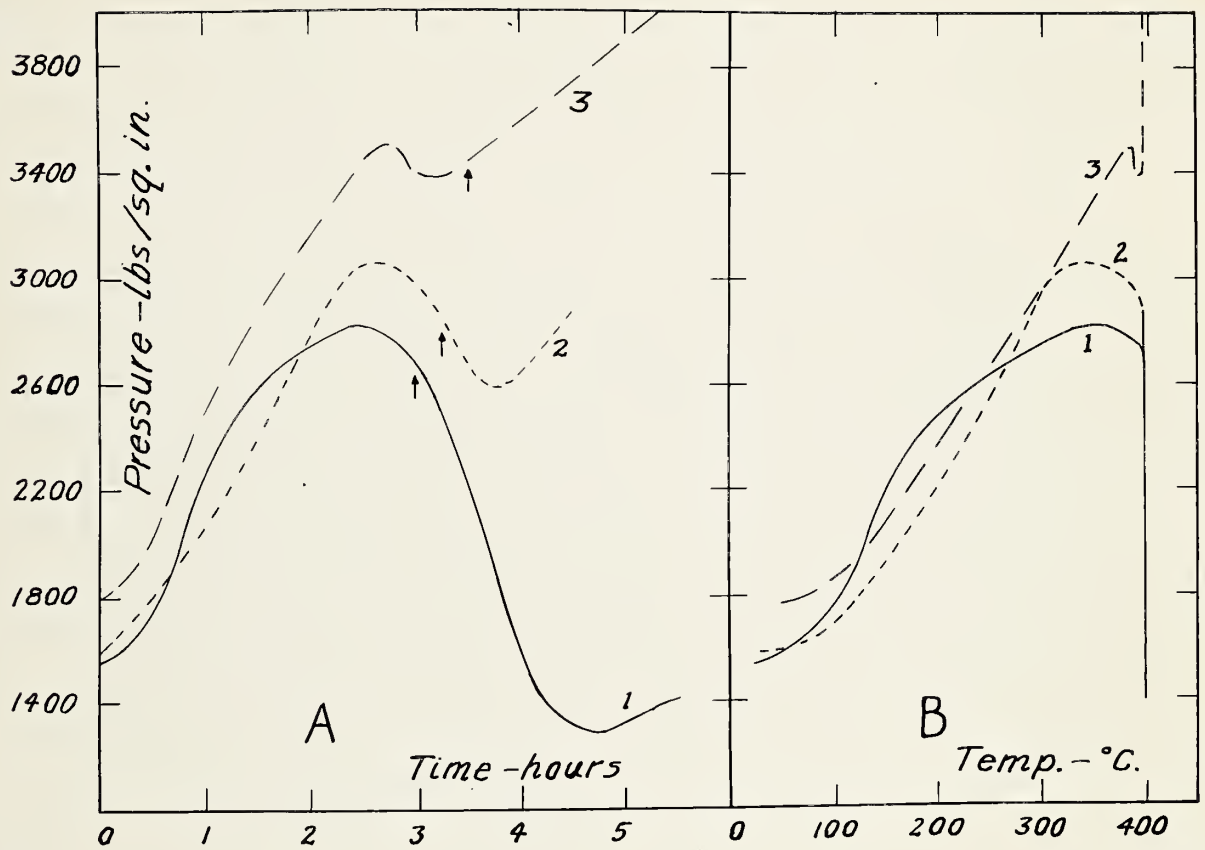


Fig. 4. Experiment No. 58: A Time-Pressure Relations,
 Temperature-Pressure Relations

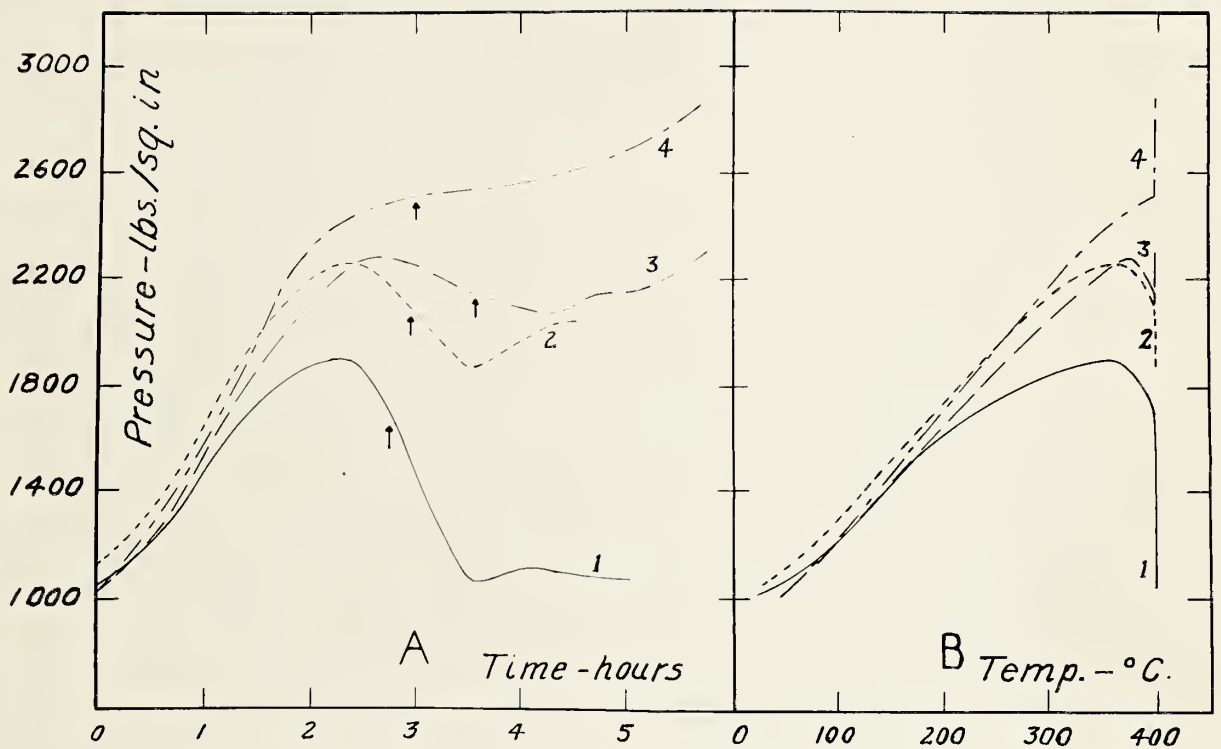


Fig. 5. Experiment No. 64. A:- Time Pressure Relations, B. Temperature Pressure Relations.

these calculations. An inspection of curves B₁, figures IV and V shows that hydrogenation of fresh bitumen begins at 100 to 150° C. and that rapid hydrogenation occurs above 300° C. In succeeding cycles (curves B₂) the initial stages of hydrogenation commence at slightly higher temperatures. The pressure measurements are not at present sufficiently precise to define this temperature with any great exactness. These curves end in a vertical line which represents the condition of constant temperature. In the first three cycles the pressure is dropping as the temperature is rising and at constant temperature the pressure continues to drop. In the fourth cycle there is no drop in pressure, merely a small inflection in the curve, followed by a rising pressure at constant temperature. This indicates a considerable effect on the reaction with hydrogen of increasing quantities of light hydrocarbons in the oil.

The curves, A, of figures 4 and 5 show clearly the rate and to some extent the degree of hydrogenation. The time at which the temperature reached the constant reaction value is shown by an arrow on each curve. Evidently rapid hydrogenation commences below 350°C. The rate of temperature rise is nearly constant but the pressure time curve rapidly flattens out near 350°C., passes through a maximum and dips to a minimum. Some regular differences in these pressure time curves are evident in succeeding cycles. The magnitude of the pressure drop and the rate of pressure drop become less as the bitumen becomes hydrogenated. Moreover, the width of the minimum region decreases and the rate of pressure increase subsequent to the minimum value increases with

successive cycles. This is not unexpected in view of the greater probability of cracking as the bitumen becomes hydrogenated.

The greater part of the hydrogen absorption occurs during the hour previous to the attainment of reaction temperature and the hour immediately after. A marked retardation in the rate of pressure drop occurs thereafter. These facts in conjunction with the previous remarks on the pressure temperature curves and the differences between successive cycles, suggest the presence of an equilibrium between the complex bitumen molecules and hydrogen on one side and the smaller hydrocarbon molecules resulting from the reaction on the other. As hydrogen reacts with bitumen, its concentration falls and this decrease is accelerated by the addition to the gas phase of volatile hydrocarbons formed from the bitumen. Then, in a single cycle it might be expected that the rate of reaction would decrease with time. In successive cycles, also, the maximum rate of reaction and the duration of hydrogenation would be expected to decrease with time. An equilibrium as described is probable and somewhat similar ideas have received attention before (27) in dealing with cracking still reactions. In the experiments under review the equilibrium will be complicated by cracking reactions and a constant equilibrium pressure is not to be expected. Fresh bitumen behaves not infrequently in this manner however, as an inspection of curve A1 of figure 5 will show. A study of the effect of hydrogen concentrations and the removal of light hydrocarbons as formed should throw light on this matter. Preliminary work along these lines is presented below.

A comparison of the slopes of curves A of Figures IV and V is of interest in bringing out the effect of a catalyst. Experiment no. 58 was carried out in the presence of molybdic anhydride and no catalyst was present in Experiment no. 64. The slopes of the decreasing pressure portion of curves A1, Figures IV and V, differ greatly. The slope in the first case is approximately 1,100 lbs. per hour as compared to 700 lbs. per hour in the second case. The corresponding values for the second cycles of these experiments are 580 lbs. and 300 lbs. per hour, respectively. Evidently the presence of a catalyst is beneficial in increasing the velocity of hydrogenation. The indications of a slow hydrogen absorption in the region of 150°C. to 200°C. point to the desirability of further experiments with catalysts of greater activity than molybdic anhydride.

The general shape of these curves is also of interest from the point of view of the mechanism of the hydrogenation reaction. Waterman and his associates (26) have postulated that the hydrogen merely produces a more uniform splitting of the complex hydrocarbon molecule. Very little of the hydrogen is absorbed at unsaturated linkages. In such a case one would expect no great decrease in the hydrogen pressure. But a large decrease is very obvious in all of this work. Evidently the hydrogen is absorbed at unsaturated linkages produced by the thermal decomposition of the bitumen molecules. The reaction mechanism of Bergius, Kling and Florentin (17) and others would seem to be much more tenable from an examination of these results.

2. Hydrogenation at 400°C. to 445°C. on 700 gr. to 1200 gr. charges.

The data of representative experiments covering the temperature range 400°C. to 445°C. are shown in Table IV. Because of the extensive cracking that occurred at these higher temperatures, the charge was reduced by stages to 700 gr. It was expected that the maximum pressure would be reduced and that the available hydrogen would be maintained at a higher concentration. Coke production and cracking were decreased by this procedure and hydrogen absorption was increased. The suppression of cracking in the presence of a sufficient supply of hydrogen at 400°C. is brought out clearly by the absence of coke in experiment no. 63. The gasoline yield is reduced, however, relative to the yield in experiment no. 64 of Table II.

Experiment no. 71 was designed to illustrate the effect of a low initial hydrogen pressure and is only of partial value because of a leak that occurred in one cycle. This caused a loss of volatile material and an increased coke production. There is, however, a decided drop in gasoline production as compared with experiment no. 64 which is, in part, real. The loss in gasoline due to the leak would be balanced to some extent by that produced in cracking to coke.

Three experiments, no. 74, no. 75, and no. 84, on 900 gr. charges and one, no. 86, on a 700 gr. charge are reported for 425°C. The first two experiments are almost identical in most respects except with regards to the gas analysis. Inexplicable variations in the gas analyses from different experiments frequently occurred. However, the

TABLE IV.

HYDROGENATION OF BITUMEN IN 700 TO 1200 GR. CHARGES AT 400 C. TO 450 C. WITHOUT ADDED CATALYSTS.

Experiment no.	68	71	74	75	84	86	83	85
Bitumen, gr.	900	1200	915	910	885	710	910	710
Number of cycles	4	3	3	3	2	2	1	1
Time, hours per cycle	3.5	2.5	2.5	3.0	1.5	1.5	1.0	2.0
Average temp. °C.	400	400	425	425	425	425	445	440
Average initial pressure lbs. per sq. in.	1060	775	1155	1145	955	1000	1000	1000
Average maximum pressure lbs. per sq. in.	2238	2210	2675	2015	2190	2375	3960	2875
Average final pressure lbs. per sq. in.	500	440	555	580	670	645	640	610
Pressure drop per cycle, lbs. per sq.in.	560	335	600	565	285	355	360	390
Hydrogen absorbed, % by weight	1.5	0.5	1.4	1.3	0.6	1.0	0.5	0.8
Gas yield, less H ₂ , litres/Kg. bitumen	54.3	44.6	106.5	89.7	55.4	77.3	66.5	87.2
Bitumen to oil, %	94.6	65.7	72.2	74.3	79.2	76.2	58.4	63.5
Bitumen to coke, %	0.0	16.7	10.4	8.2	7.9	12.0	21.8	18.4
Bitumen to gas, %	2.4	2.4	7.0	6.6	3.7	4.5	3.4	4.9
Loss, %	3.0	15.2	10.4	10.9	9.2	7.3	16.4	13.2
Bitumen to gasoline, %	17.4	17.1	32.5	37.9	25.0	29.9	29.2	31.8
Refined gasoline, %	13.9	13.6	28.3	28.2	20.6	25.1	23.4	25.6
Gas Analysis, %								
CO ₂	9.4	12.2	11.1	3.2	5.8	6.9	4.5	8.5
CnH _{2n}	0.9	2.1	1.5	1.6	1.6	2.1	10.6	3.8
H ₂	52.0	22.9	27.3	36.5	49.5	48.3	10.4	-
C ₂ H ₆	16.7	29.4	39.6	15.8	23.6	-	27.0	36.8
CH ₄	11.1	26.4	15.9	31.2	14.4	-	41.8	13.9
H ₂ S.	11.0	5.8	2.3	2.0	4.6	3.8	4.3	6.1
Oil Properties,								
Density, 25°C.	0.927	0.941	0.903	0.904	0.929	0.918	0.903	0.898
Viscosity, 25°C.	0.319	0.134	0.034	0.038	0.102	0.054	0.024	0.028
Carbon Residue %	7.3	9.4	5.7	6.1	9.5	9.4	8.6	7.0
Unsaturation %	-	40	35	34	60	44	43	42
Sulphur %	1.68	1.95	1.25	1.16	1.85	1.58	1.68	1.84
Initial B.P.°C.	68	70	36	37	44	40	27	33
Per cent. at 200°C.	16	24	39	39	27	32	43	43
Per cent. at 300°C.	38	48	65	63	51	58	65	67
End point, °C.	363	337	338	320	336	314	340	342
Percentage pitch	34	18	24	26	22	27	24	19

analyses of successive cycles in one experiment varied in a regular and expected manner. In experiment no. 84 the time per cycle was reduced by half and only two additions of hydrogen were made. There is evident a small decrease in coke yield and a large decrease in the amount of hydrogen absorbed. It may be concluded from this experiment that increasing the hydrogen concentration does not cause an acceleration of the reaction equivalent to that produced by a catalyst. The results of experiment no. 86 do not show any great differences from the preceding experiment at this temperature. Gasoline production is higher and the hydrogen absorption is greater although the time per cycle is unchanged. The oil produced is of a distinctly better quality.

In general coke production at 425°C . amounts to 10% and refined gasoline production is 25% to 30% of the bitumen, as compared to zero and 15% to 20% for the same data at 400°C .

Two experiments, nos. 83 and 85, at 445°C . and 440°C . respectively, are reported. The losses are high and detract from the value of these experiments. The gasoline production is much the same as at 425°C . and the hydrogen absorption is less. The large gas and coke production show that cracking predominated and was responsible for most of the gasoline. There is a distinct improvement in the oil quality as shown by all the properties except unsaturation. The gas analyses in these experiments are inexplicable in showing 10% or less of hydrogen and bearing little resemblance to one another.

The properties of the oils produced in this series of experiments reveal some interesting results. Generally, the

density, viscosity and initial boiling point decrease with rising temperature. The coke and gasoline yields increase rapidly between 400 and 425°C. but the increase is only slight between 425°C. and 445°C. The yield of oils boiling above 225°C. is greatly decreased as the temperature rises but their quality is greatly improved in regards to bitumen content. Kerosene and gas oil make up from 25 per cent. to 30 per cent. of the crude oils produced at 425°C. and the remainder contains 10% to 12% of the crude oil as lubricating oils and paraffin wax. This lubricating oil fraction was obtained by vacuum distillation to 325°C. Higher temperatures were not employed as decomposition commenced and a solid, high melting point wax interfered in the condenser. The pitch remaining in the still was asphaltic in nature being insoluble in hot petroleum naphtha and 99.5 per cent. soluble in carbon disulphide. The lubricating oil fraction was of a fluorescent green colour and almost transparent. The oil did not change appreciably on standing except for a slight reddening in colour. A separation of the paraffin wax content was impossible due to its poor crystal form. Chilling precipitated the wax as a green mud estimated at 50% by volume of the total fraction. A clear green supernatant oil having no fluorescence remained above the wax.

In Figure VI is presented the pressure-time and pressure-temperature relations of the three cycles of experiment no. 74 run at 425°C. The general form of these curves is the same as in the runs at 400°C. with the exception that the depression to a minimum value in Fig. VI, A, is much smaller. The pressure time curves of experiments nos. 83 and

85 at 445°C . and 440°C . are shown in Fig. VII, A. They also resemble all of the previous curves except the decrease in pressure due to hydrogen absorption is even smaller in this case. The pressure also shows a greater tendency to rise sharply after this low point, due of course, to cracking. The pressure temperature charts of these last experiments are also characterized by a shallow minimum dip followed by a steady rise at constant reaction temperature.

It would appear that the concentration of hydrogen is an important factor among the conditions governing hydrogenation and cracking. A large reduction in hydrogen concentration such as occurs through hydrogenation allows cracking to begin. The higher the temperature the smaller this allowable reduction in hydrogen concentration that will retard cracking becomes. The logical conclusion follows that a continuous process in which the hydrogen concentration can be maintained at a high value, is advisable.

An inspection of Fig. VIII, showing the pressure-time curves of experiments no. 68 and no. 74, makes it evident that hydrogenation occurs more rapidly at 425°C . than at 400°C . Only the first cycle of these comparable experiments is shown and the arrows point to the time when constant temperatures of 400°C . and 425°C . were reached. There was no leak in either of these cycles. The rate of hydrogenation as given by the slope of the curve after constant temperature has been reached, increases continually to at least 425°C . The ultimate course of the pressure-time curves differs markedly. In less than one hour at 425°C . the pressure rises steadily as cracking occurs and at 400°C . the pressure drops slowly to a constant value. A definitely increasing pressure

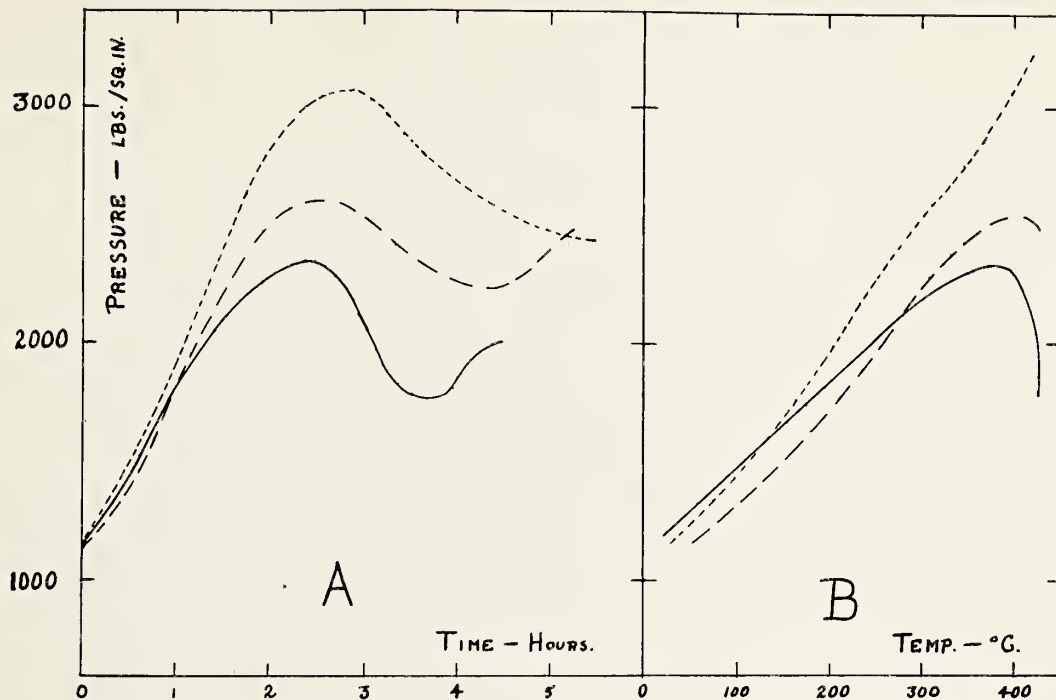


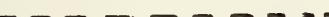


Fig. 6. Experiment No. 74. A, Time-Pressure Relations,
B, Temperature-Pressure Relations.

1st. Cycle.	
2nd. Cycle.	
3rd. Cycle.	

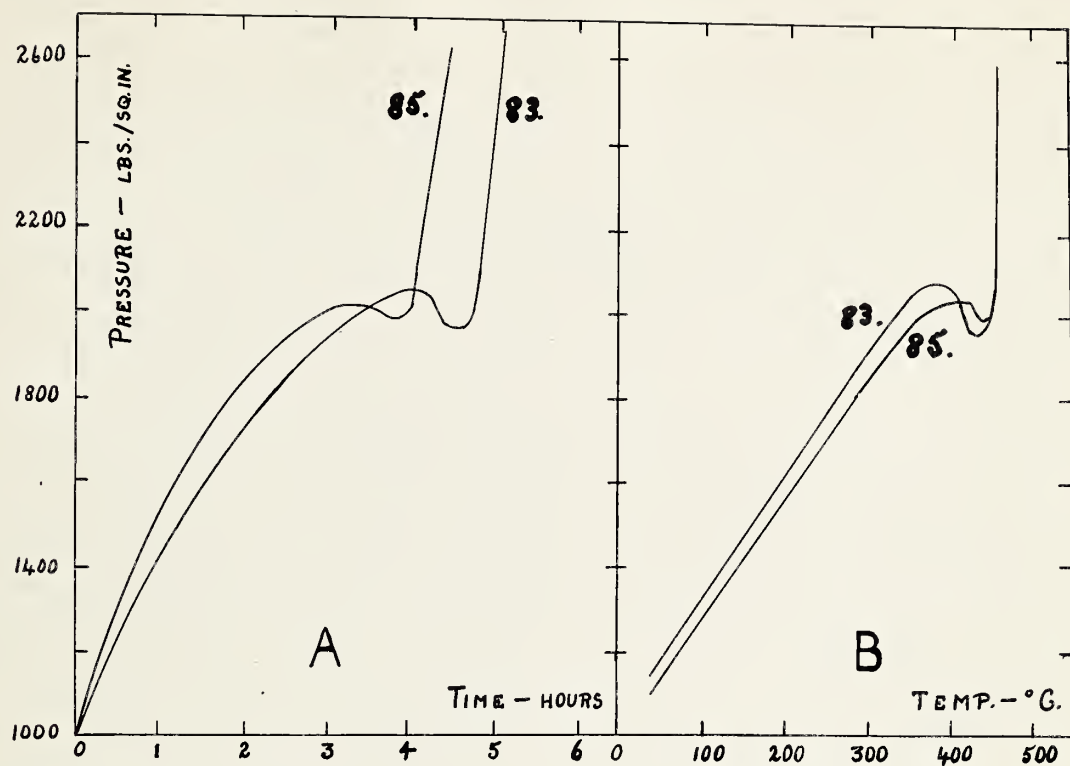


FIG. 7. Experiments No. 83 & 85. A, Time-Pressure Relations,
B, Temperature-Pressure Relations.

has not been found to occur with fresh bitumen at 400°C . in the absence of leaks. With partially hydrogenated bitumen such as is present in the second and succeeding cycles at this temperature cracking occurs and the pressure rises indefinitely.

Some indication of the effect of an increased hydrogen concentration on this reaction is brought out in Fig. IX which shows the pressure-time relations of the first cycle of experiments no. 64 and no. 68. Both were run under practically identical conditions of temperature and pressure; namely 400°C . and an initial hydrogen pressure of 1100 lbs. per sq. in. However, in experiment no. 64, 1200 gms. of bitumen were used and 900 gms. in experiment no. 68. The rate of hydrogen absorption as measured by the pressure drop per hour is much more rapid in the case of the experiment with the larger charge. In no. 64 the hydrogen pressure is rapidly reduced to the minimum value at which cracking occurs and the pressure starts to rise. This latter effect does not appear in the case of the 900 gm. charge. This behaviour is due to the relative amounts of hydrogen and bitumen in the reaction chamber. In experiment no. 64 the smaller volume of hydrogen is rapidly used up by the 1200 gms. of tar. In no. 68 however, there is present a larger volume of hydrogen which, although absorbed at about the same absolute rate as in no. 64, shows a much more gradual decrease in pressure with time. The minimum pressure value at which cracking occurs is not reached by the duration of this experiment.

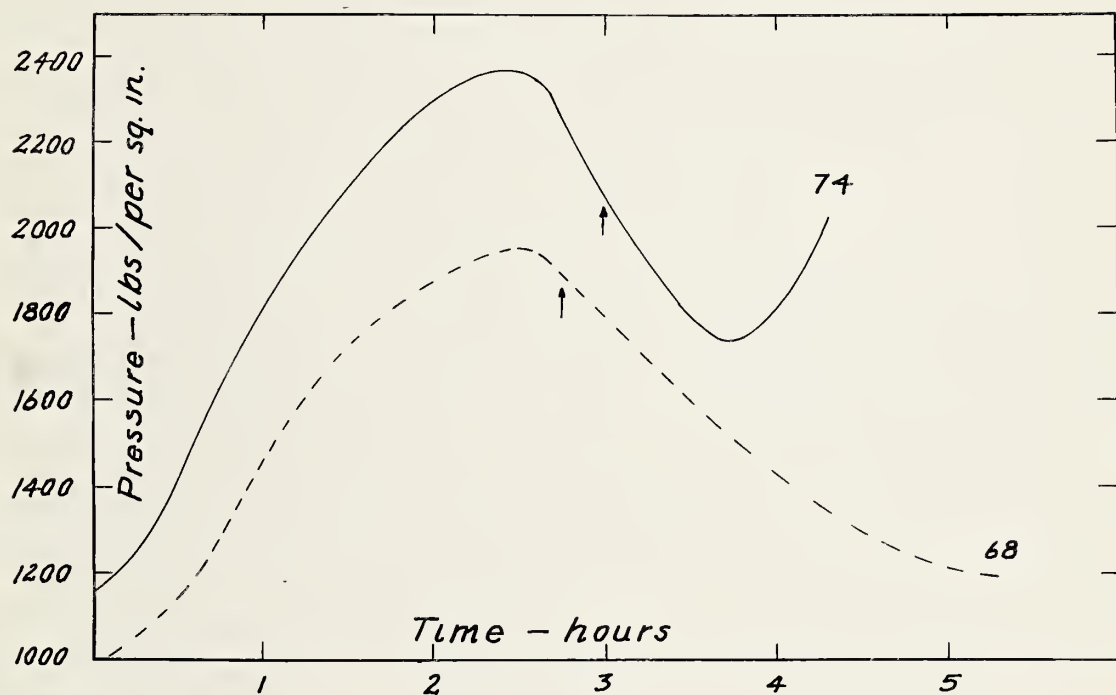


Fig. 8. Pressure-Time Relations of First Cycles of Experiments
NO. 68 & 74.

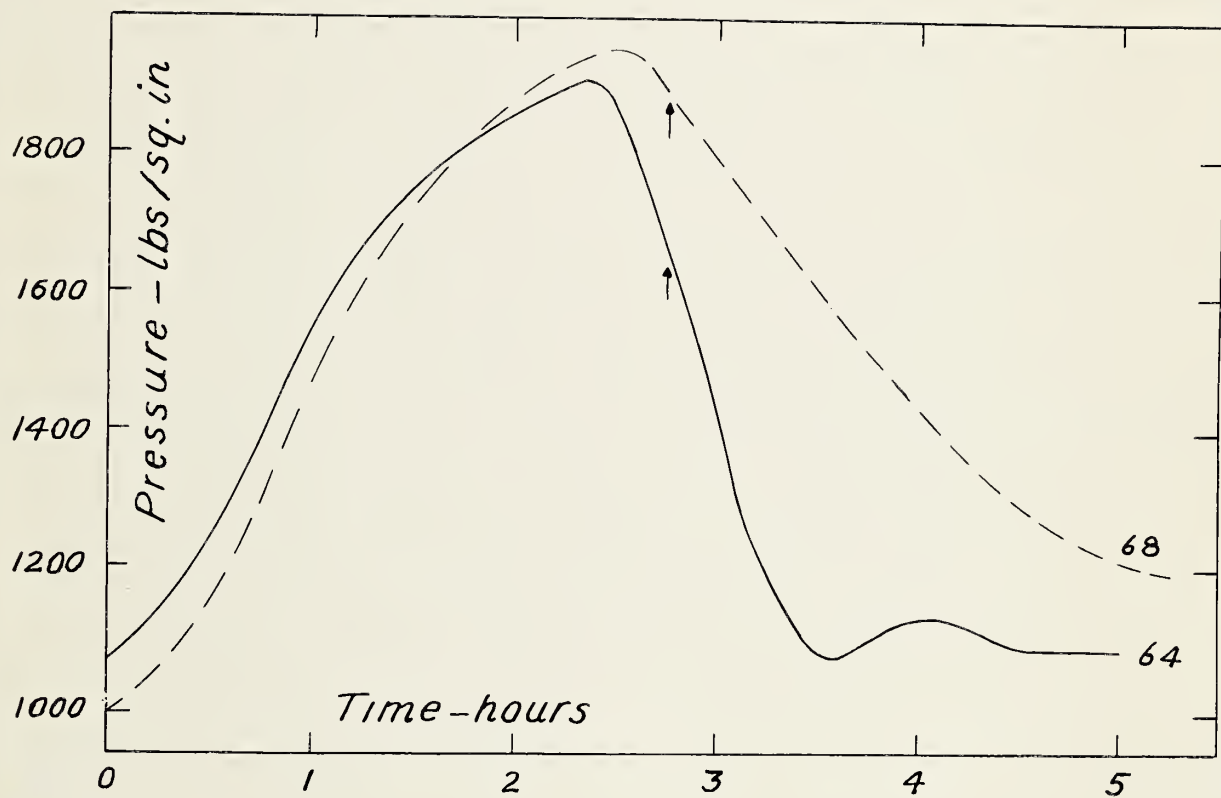


Fig. 9. Pressure-Time Relations of First Cycles of Experiments No. 64 and No. 68.

3. Hydrogenation with 400 gr. charges of bitumen.

To investigate further the effect of the amount of available hydrogen a number of experiments were carried out using approximately 400 gr. charges of bitumen at temperatures of 400°C., 425°C. and 450°C. There was available a volume of hydrogen equal to 1200 c.cm., more or less, which at the common initial pressure weighed about 10 gr. or 2.5% of the bitumen. Two of the six experiments reported were run with a catalyst; in one case, 5 per cent. of molybdic anhydride and in the other, 4.4 per cent. of ammonium molybdate. Only one cycle was carried out in each experiment and the time of reaction was four hours at 400°C. and 425°C. At 450°C. the time was shortened to two or three hours because of excessive cracking. Table V presents the details of these experiments and shows beyond doubt the beneficial effect of increased available hydrogen.

Coke production is very much decreased and the light oil fraction boiling below 300°C. is as much as 40% of the original bitumen on one addition of hydrogen. The hydrogen absorption is as great in one cycle as that obtained previously in several cycles. In these experiments no leaks occurred and the recorded losses must be assigned to a poor recovery of liquid and, to a small extent, gaseous products. The loss of solid products may be considered as negligible and the error in the determination of gaseous carbon cannot be more than 2 per cent. The high losses reported in experiments no. 104, no. 107 and no. 108 at 450°C. can only be due to the evaporation of volatile hydrocarbons while recovering

TABLE V.

HYDROGENATION OF BITUMEN IN SMALL CHARGES AT 400°C. TO 450°C.

Experiment no.	106	105	109	104	107	108
Bitumen gr.	475	462	400	461	375	455
MoO ₃ , %	0	0	5.0	0	0	0
(NH ₄) ₂ MoO ₄ , %	0	0	0	0	0	4.4
Number of cycles	1	1	1	1	1	1
Time, hours per cycle	4	4	4	2	3	2
Average temperature °C.	400	425	425	450	450	450
Average initial pressure, lbs./ sq. in.	1325	1280	1145	1280	1280	1190
Average maximum pressure, lbs./ sq. in.	2570	2148	1963	2524	2380	2290
Average final pressure, lbs. / sq. in.	910	645	485	720	755	695
Pressure drop, lbs. / sq. in.	415	635	660	560	525	495
Hydrogen absorbed, % by weight	0.7	1.1	1.5	1.4	1.3	1.2
Gas yield, less H ₂ , litres/ Kg. bitumen	47.4	81.3	91.0	159.0	192.0	131.0
Bitumen to oil, %	92.7	79.2	85.0	51.0	54.7	57.2
Bitumen to coke, %	0.0	7.6	0.0	11.9	6.7	15.4
Bitumen to gas, %	2.9	5.3	5.1	10.0	12.8	9.1
Loss, %	4.4	7.9	9.9	27.1	25.8	18.3
Bitumen to gasoline, (A.S.T.M) %	11.1	25.4	29.0	-	28.4	29.2
Gas Analysis, %						
CO ₂	3.1	3.8	7.4	3.6	5.3	4.9
CnH _{2n}	1.5	2.3	2.3	2.2	3.4	2.3
H ₂	75.5	46.7	35.9	29.4	36.5	30.4
C ₂ H ₆	4.5	25.8	28.0	37.4	34.2	45.3
CH ₄	9.1	9.5	14.9	19.2	15.5	11.9
H ₂ S	3.6	6.0	6.6	-	1.3	-
Oil properties,						
Density, 25°C.	0.955	0.925	0.911	-	0.916	0.908
Viscosity, 25°C.	-	0.088	0.069	-	0.028	0.030
Carbon residue, %	10.5	8.0	11.9	-	10.5	8.4
Unsaturation %	78	48	42	-	42	35
Sulphur %	2.53	1.95	1.76	-	2.11	2.25
Initial B.P. °C.	72	57	60	-	47	46
Per cent. at 200°C.	9	24	27	-	45	44
Per cent. at 300°C.	27	52	54	-	65	67
End point °C.	340	345	332	-	355	363
Per cent. pitch	47	30	32	-	25	21

the oily products which were much lighter than any encountered in previous work. Substances such as butane and pentane are probably formed in large amounts in all of this work. Some can be recovered from the gas but no doubt the greater part is lost during the removal of the oil from the autoclave. The conversion of bitumen to gaseous hydrocarbons is very large in all of this set of experiments. At 400°C. and 425°C. it is of the same order as that produced in the series on larger charges after several cycles and at 450°C. it is much greater. It would appear that the conversion to gaseous hydrocarbons is controlled by the concentrations in the gas phase of the reactants as well as by temperature and time. A relation between the degree of hydrogenation and the production of gaseous hydrocarbons is to be expected if an equilibrium exists. Consequently the gas production would not depend on the number of cycles but on the equilibrium concentrations of the various reactants and the volume of the gas phase.

The addition of molybdic anhydride at 425°C. accelerates the reaction and permits the complete suppression of coke formation. An increased hydrogen absorption and gasoline production is also apparent in experiment no. 109. The quality of the crude oil shows a slight improvement when compared to that produced in experiment no. 105. The use of ammonium molybdate at 450°C. does not appear to be entirely beneficial in view of the increased coke production in experiment no. 108 compared to no. 107. The gas yield and the production of volatile hydrocarbons in the presence of this catalyst show a decided decrease and the oil is of a

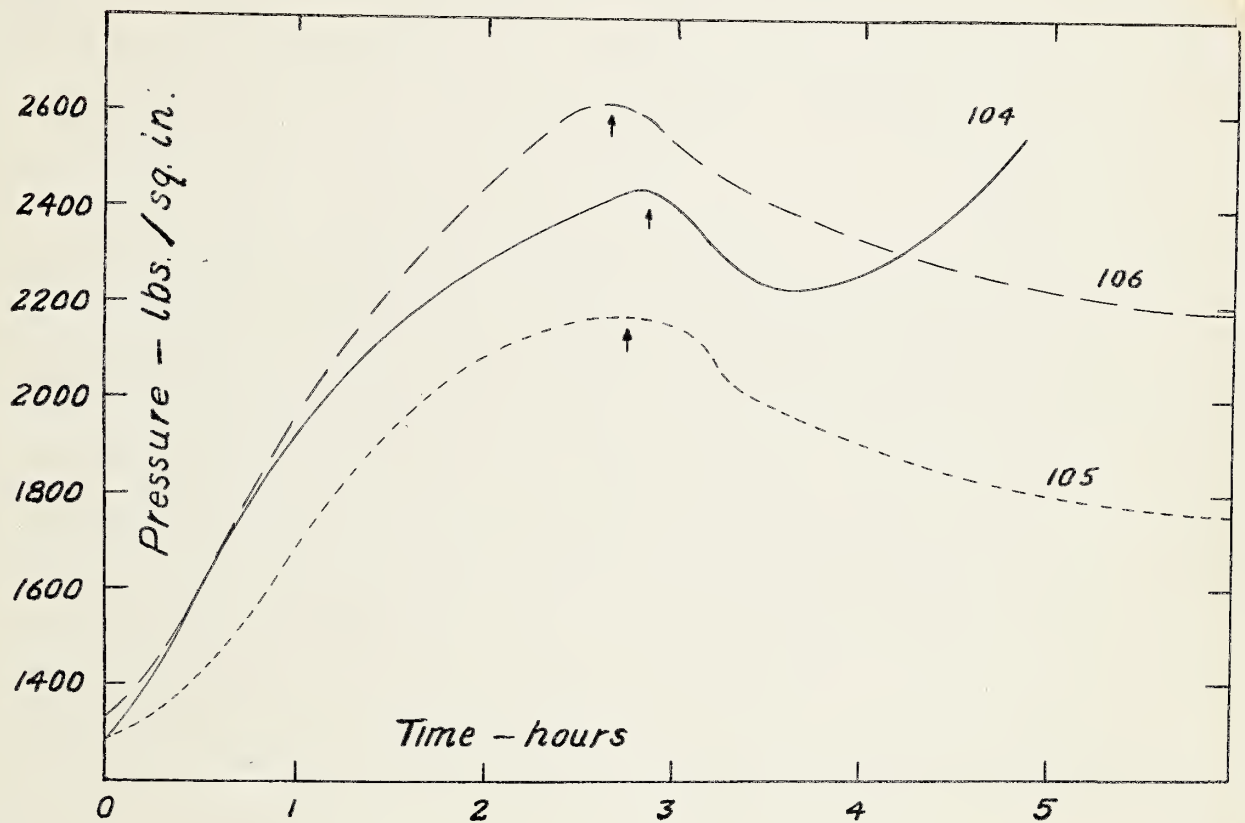


Fig. 10. Pressure-Time Relations of First Cycles of Experiments No. 104, No. 105 and No.106.

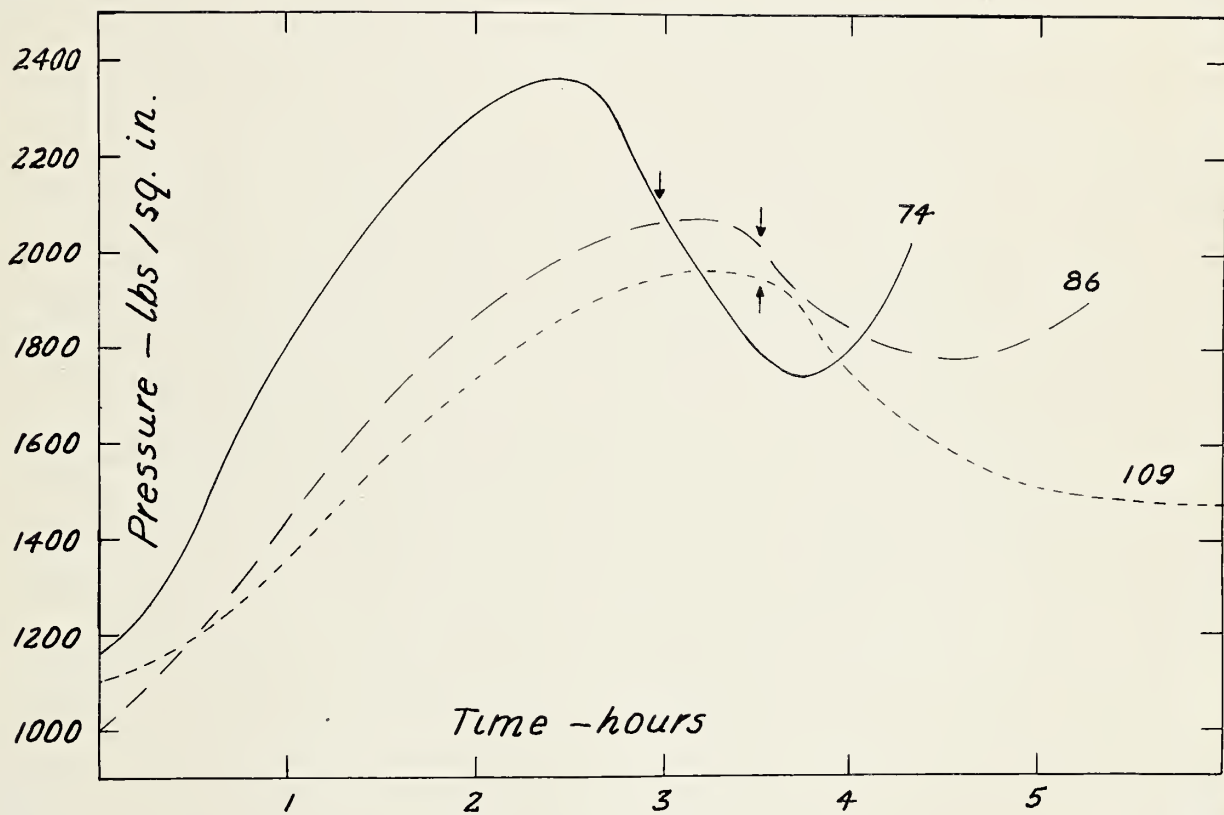


Fig. 11. Pressure-Time Relations of First Cycles of Experiments No. 74, No. 86 and No. 109.

better quality. On the whole, no decision can be made at present as to the value of a catalyst for this reaction at 450°C.

The pressure-time curves of experiments no. 104, no. 105 and no. 106 are shown in Fig. X. It is evident that the rate of hydrogen absorption increases with rising temperature and only at 450°C. does cracking occur in such a manner as to lead to an ultimate pressure rise. This is contrary to usual experience at 425°C. with larger charges of bitumen (Figure VI). To illustrate clearly the effect of available hydrogen Figure XI is shown in which are the pressure-time curves for the first cycles of experiments no. 74, no. 86 and no. 109. These experiments were all performed at 425°C. and differed in the weight of charge used, being 915 gr., 710 gr. and 400 gr. respectively. The maximum pressure developed, taking into account the differing initial pressures, drops by approximately 70 lbs. per sq. in per 100 gr. decrease in weight of charge. The rate of hydrogen absorption as given by the average slope of the curves in the decreasing pressure region is 520 lbs. per hour for experiment no. 74, 235 lbs. per hour for experiment no. 86 and 360 lbs. per hour for experiment no. 109. The absolute rates of hydrogen absorption in gr. of hydrogen per gr. of bitumen per hour are in the ration 0.4:0.3:1.0. for the experiments in the order named above. Evidently there is a distinct saving in time to be gained in the use of relatively large amounts of hydrogen whereby the hydrogen concentration is maintained at a high figure.

The similarity of these reactions to those of preceding sections is brought out in Fig. XII in which the

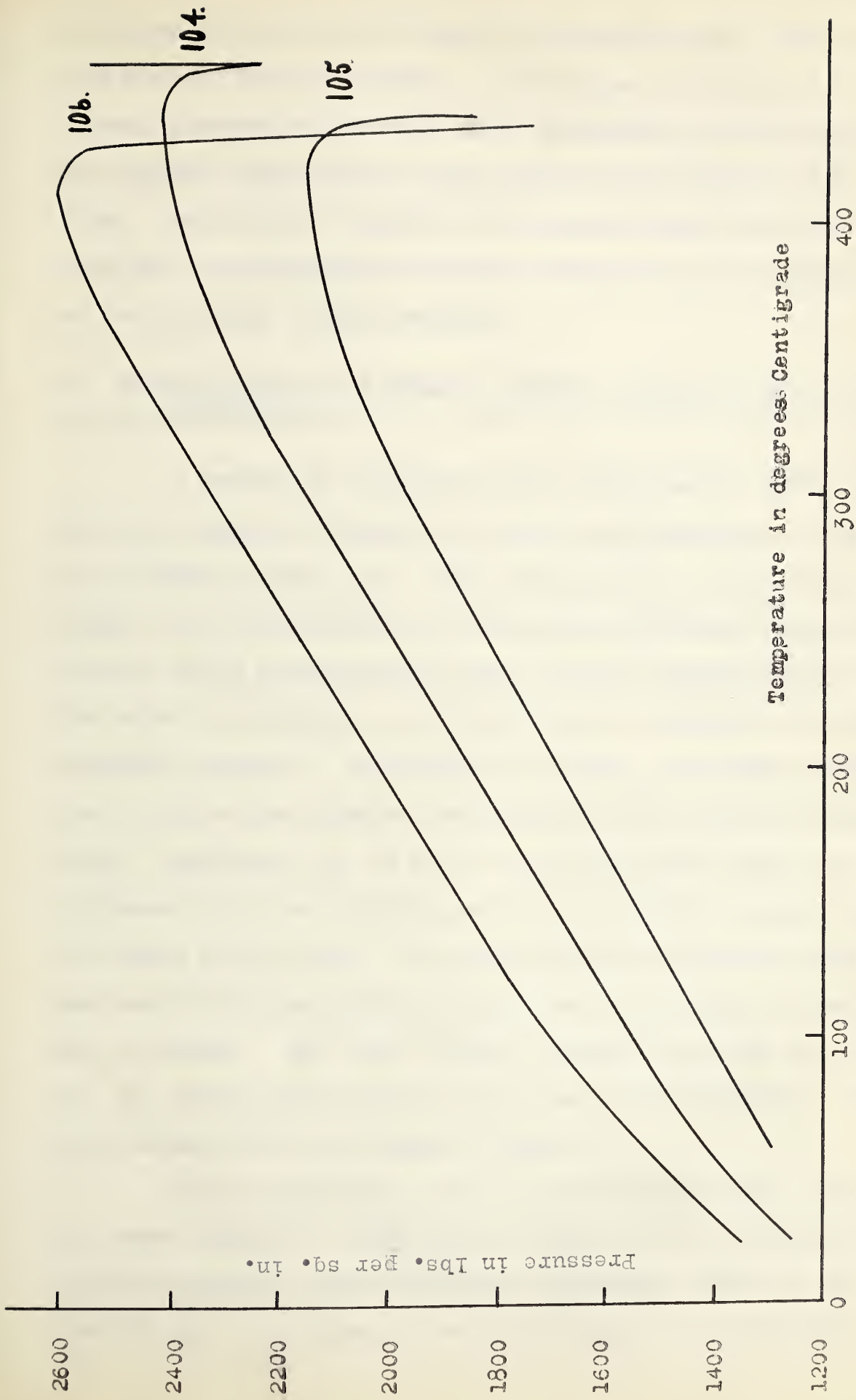


Fig. XII Pressure-temperature relations of expts. 104, 105, 106.

pressure-temperature relations of experiments no. 104, no. 105 and no. 106 are plotted. In the last two of these a steady increase of pressure with temperature is recorded and at constant temperature a slow decrease in pressure with time. The initial behaviour of experiment no. 104 is the same but the decrease at constant temperature is followed by an indefinitely rising pressure.

4. Hydrogenation at different initial partial pressures of hydrogen.

A number of experiments were performed at 425°C. on 900 gr. charges of bitumen in which the hydrogen was diluted with Viking natural gas. These experiments had for their object the determination of the minimum hydrogen concentration at which hydrogenation would proceed satisfactorily. Two other experiments, no. 89 and 90, are included for comparative purposes. Experiment no. 89 was a straight cracking run in which the pressure developed was the thermal pressure only. Experiment no. 90 was of the same nature with the difference that an initial pressure of 400 lbs. per sq. in. of Viking gas was used. The other three experiments were started with three different mixtures of hydrogen and natural gas as tabled. The total initial pressure was 1000 lbs. per sq. in. in each case and one cycle only was conducted. The experimental data are shown in Table VI.

These experiments are of a preliminary nature only and serve merely as indications of what is to be expected. Other experiments under different conditions remain to be carried out. At present more information can be obtained

from the results of the work reported in previous sections on the effect of hydrogen concentrations.

The experiments no. 89 and no. 90 are very similar in many respects. The effect of the natural gas added in the second experiment appears in a reduction of the conversion of bitumen to gas and volatile hydrocarbons. The crude oil is heavier, more viscous and less volatile. The remarkable similarity of the gas produced in these experiments is hardly to be expected. The effect is not new and has been found in other work, using various pressures of natural gas. However, these latter experiments were conducted in the Cook autoclave, and are not entirely trustworthy. That the final relative partial pressure of methane should be independent of the initial pressure, suggests a reversible equilibrium between the gaseous and liquid products of the cracking process such as proposed by Wilson (27).

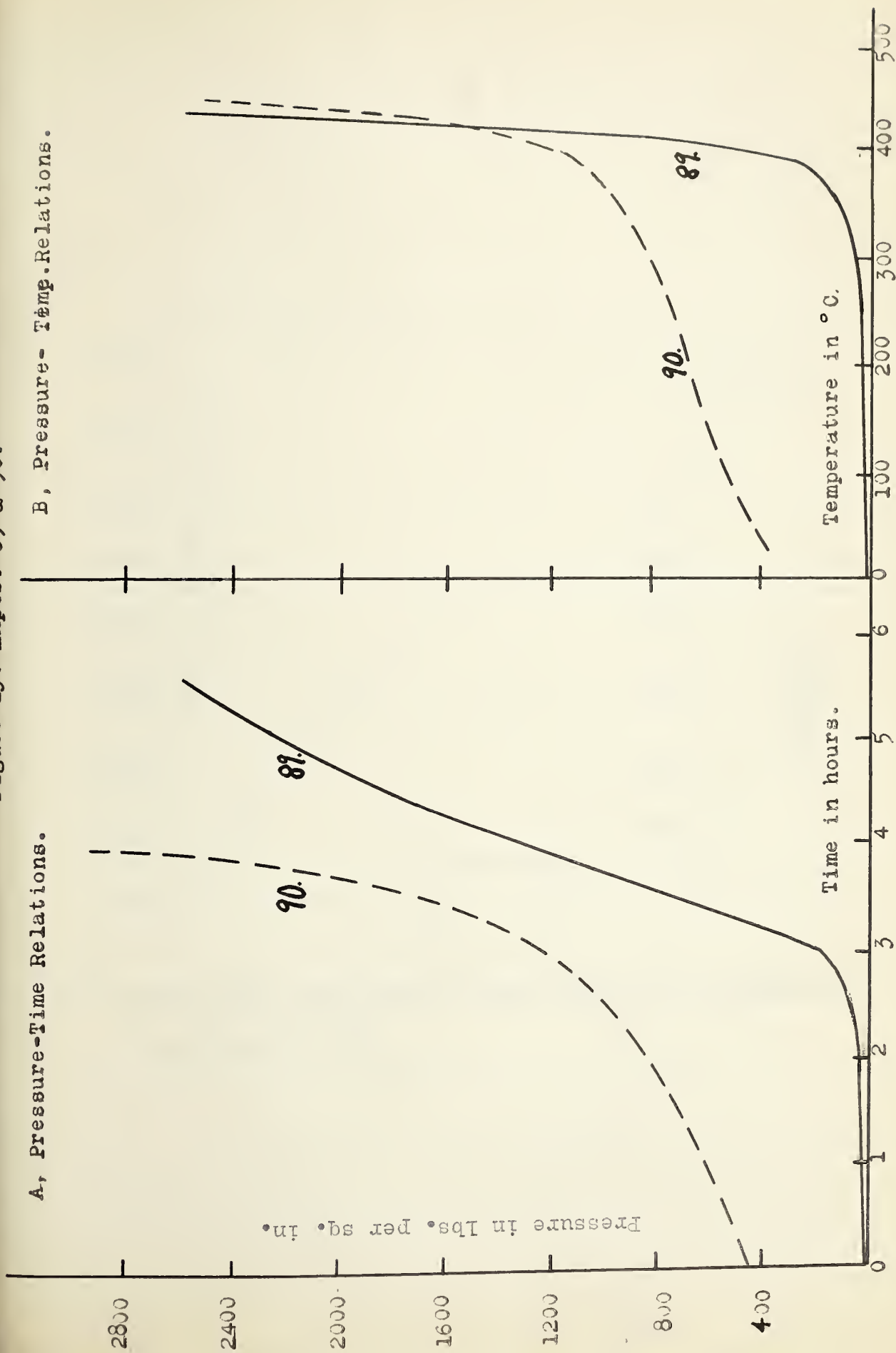
The high boiling point of the bitumen was very clearly shown in experiments such as 89. The pressure becomes appreciable, (about 25 lbs. per sq. in), at 370°C. As in Fig. XIII (B) the pressure rises only slightly faster than the temperature until 400°C. where decomposition apparently sets in. The pressure rises thereafter at the rate of 700 lbs. per hour. at any temperature between 400°C. and 425°C. A similar behaviour is also noticed in the characteristic pressure-time curve of this figure. The sulphur content of the gas is remarkably high and exceeds the quantities common in hydrogenation experiments. Apparently the conversion of sulphur in the bitumen to hydrogen sulphide is not due to hydrogenation but is the result of pyrolytic decomposition.

TABLE VI

HYDROGENATION OF BITUMEN AT VARIOUS HYDROGEN CONCENTRATIONS IN ONE CYCLE

Experiment no.	89	90	92	91	93
Bitumen gr.	925	925	920	900	900
Temperature°C.	420	425	425	425	425
Natural gas. lbs./sq. in.	15	400	333	500	667
Hydrogen. Lbs./sq.in.	0	0	667	500	333
Total initial pressure, lbs./sq. in.	15	400	1000	1000	1000
Maximum pressure, lbs./sq. in	2560	2920	3120	3900	3700
Final pressure, lbs./sq. in	650	810	800	840	1080
Pressure drop, lbs./sq. in	-635	-410	200	160	-80
Time, hours	2	1	1.5	1.5	1
Hydrogen absorbed, % by weight	-	-	0.4	0.2	0.2
Gas yield, less added gases litres 1 Kg. bitumen	49.3	-	57.1	-	59.5
Bitumen to oil %	63.8	68.1	73.9	68.4	74.0
Bitumen to coke %	18.9	18.9	16.3	18.9	15.5
Bitumen to gas %	3.2	-	3.3	-	3.2
Loss %	14.1	8.4	5.4	7.3	5.1
Bitumen to gasoline %	26.0	25.0	26.9	27.9	28.7
Refined gasoline %	20.1	21.5	22.6	23.0	24.0
Gas Analysis %					
Co ₂	7.3	8.6	9.7	8.2	6.4
CnH _{2n}	3.0	2.9	2.3	2.9	2.1
H ₂	3.0	0.0	6.0	3.1	6.3
C ₂ H ₆	45.5	42.7	41.7	33.4	34.4
CH ₄	32.0	32.5	31.0	42.4	42.7
H ₂ S	5.7	5.1	4.4	3.3	3.4
Oil properties					
Density, 250°C.	0.926	0.936	0.931	0.919	0.933
Viscosity, 25°C.	0.056	0.09	0.072	0.048	0.101
Carbon Residue, %	11.4	12.0	9.6	10.2	11.4
Unsaturation %	38	62	57	66	57
Sulphur %	2.90	3.03	2.87	2.87	2.98
Initial B.P. °C.	40	43	37	36	42
Per cent. at 200°C.	34	29	29	36	27
per cent. at 300°C.	59	54	54	59	51
End point, °C.	335	318	340	338	336
Per cent. pitch	22	37	29	24	31

Figure 13. Expts. 89 & 90.



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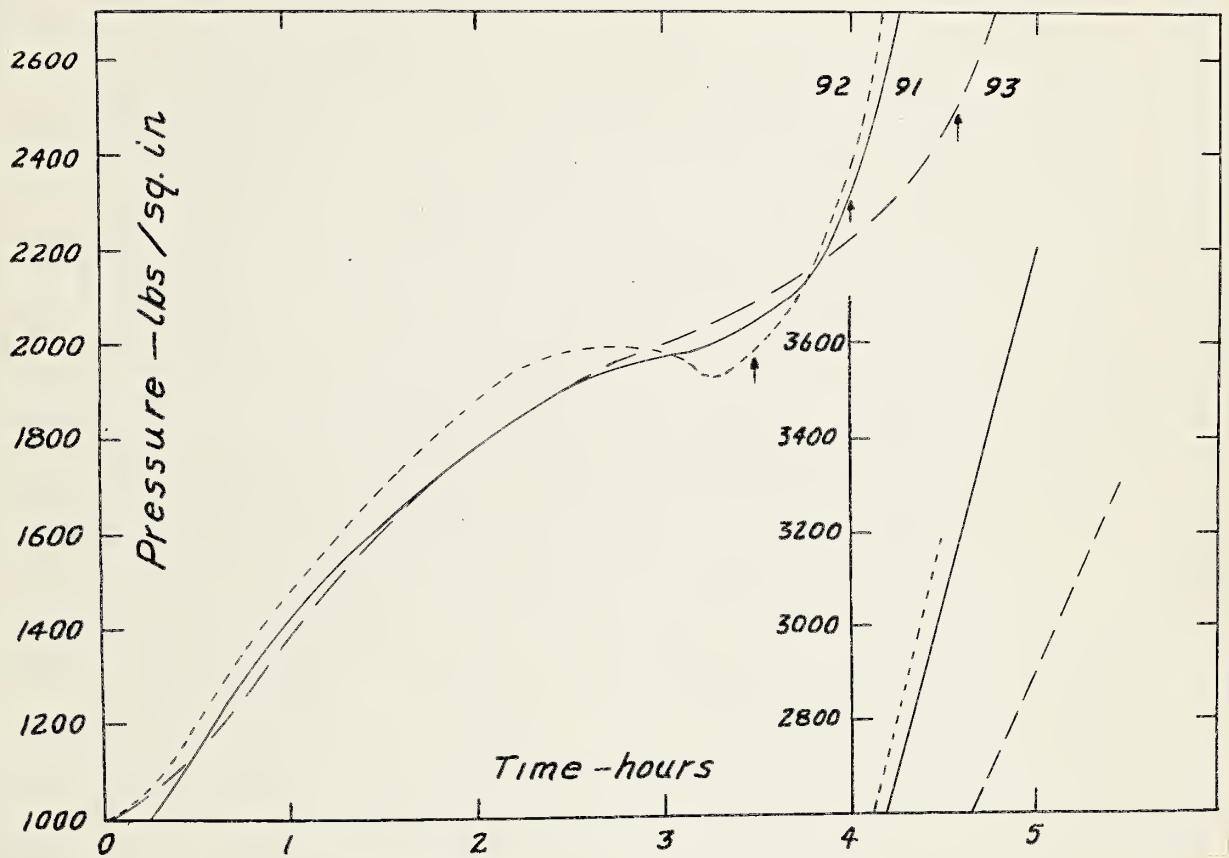


Fig. 14. Pressure-Time Relations of First Cycles of Experiments No. 91, No. 92 and No. 93.

Hydrogenation may have an adverse effect by increasing the stability of the sulphur compounds. A definite statement cannot be made on the basis of two experiments only.

Referring to experiments no. 91, no. 92, and no. 93 it is at once evident that reduction of the hydrogen concentration has a profound effect on the reaction. The oil yields are down and the coke yields are up compared to the experiments of Table IV. The pressure time curves shown in Fig. XIV illustrate graphically the decrease in hydrogen absorption. Only in experiment no. 92, using 66.7% hydrogen, is a pressure drop evident. Under the conditions of these experiments an initial hydrogen concentration greater than 50% is necessary for appreciable hydrogenation. The lower limit is undoubtedly less than 50% in the light of residual gas analyses; but this lower limit is rapidly reached when the initial hydrogen concentration is about 50 per cent.

The results of the oil and gas analyses do not show any marked differences between these experiments. Experiment no. 93 does show a greater resemblance to experiments no. 89 and no. 90 than to the other two. Moreover the maximum and final pressures, hydrogen absorption, coke production, gas yield and gas analysis definitely separate experiment no. 92 from no. 91 and no. 93.

5. Hydrogenation of residual oils and pitch.

The success of a continuous process for the hydrogenation of bitumen will depend on two experimental factors. First, the hydrogen concentration has been discussed above. The second involves the reduction of all the bitumen to oils

without coke formation in serious amount. Preliminary to the establishment of apparatus in which hydrogen and bitumen may be added and the products of the reaction withdrawn in a continuous manner, experiments were carried out on oils and pitches remaining after distillation of the crude oils produced in the experiments reported. These residual oils and pitches contain all of the asphaltenes, tar acids and bases and high boiling point hydrocarbons not removed by the distillation process. They also contain those portions of the original bitumen most resistant to hydrogenation. Hydrogenation of these residues should indicate the possibilities of a continuous process by giving information as to the total probable conversion to oil.

The experimental details are given in Table VII. A variety of residues were employed and their origin is given by the first figure of the experiment number. This figure refers to the tables of previous sections in which are given the history and properties of the crude oils serving as sources of the residues under consideration. The crudes listed in these tables together with those of the same series not listed, were distilled to various temperatures at different pressures and the residues combined to make up the charges of the experiments on Table VII. The temperature and the pressure at which distillation ceased is tabled for each experiment under "Initial B.P. of charge". The amount of residue is referred back in each case to the bitumen from which it was derived. This figure is approximate only and is tabled as "Per cent. of original bitumen". An approximate calculation has been tabled in the last row of Table VII

TABLE VII
HYDROGENATION OF RESIDUAL OILS AND PITCH.

Experiment no.	4.1	4.2	5.1	2.1	2.1A	2.2	4.3	4.3A	2.3
Charge gr.	925	725	350	1200	900	408	385	257	347
Catalyst, %.	-	-	5	-	-	5	5	5	7
Compound			MoO ₃			MoO ₃	MoO ₃	MoO ₃	AlCl ₃
Initial B.P.) °C.	225	225	300	250	65	250	325	-	250
of Charge.) mm. Hg.	700	700	700	25	700	25	25	-	25
Percent. of original bitumen	50	34	36	38	38	36	15	15	22
Number of cycles	2	1	1	4	3	1	1	1	1
Time, hours/cycle	3	3	3	3.5	3.3	1.5	3	1	2
Average temperature °C.	420	450	450-	400	425	470	450	500	460
Average initial pressure lbs. per sq. in.	1000	1000	1055	1150	1200	1020	1020	1055	1100
Average maximum pressure, lbs. sq. in.	2185	2890	2055	2120	2590	1960	1825	1970	1960
Average final pressure, lbs. per sq. in.	770	800	595	445	550	750	490	625	495
Pressure drop per cycle, lbs. sq. in.	230	200	460	705	650	270	530	430	605
Hydrogen absorbed % by wt.	0.5	0.5	1.3	1.0	1.3	1.3	1.5	2.2	1.9
Gas yield, less H ₂ litres / kg. charge.	37.6	85.0	84.0	37.1	67.0	139.0	104.0	180.0	118.0
Oil yield, %	86.3	73.9	86.7	92.0	74.5	40	71.4	69.3	53.0
Coke yield %	0.0	0.0	2.2	2.8	12.8	31	0.0	Small	25.7
Gas yield %	2.0	4.8	3.5	1.7	3.3	7.9	4.5	7.8	7.4
Loss, %	11.7	21.3	7.6	3.5	0.0	21.1	24.1	20.9	13.9
Gasoline yield %	15.8	16.7	21.0	15.5	22.6	10.0	-	-	13.8
Gas analysis %									
Co ₂	1.6	2.6	0.4	7.0	4.2	1.1	1.2	0.9	0.1
CnH _{2n}	1.4	2.4	0.8	1.1	1.2	0.3	0.9	1.7	0.3
H ₂	61.9	20.8	55.3	20.4	43.2	29.8	31.2	34.8	35.0
C ₂ H ₆	16.0	29.1	15.4	22.0	22.0	29.2	19.4	28.2	33.6
CH ₄	11.7	40.4	14.8	32.6	13.8	29.1	28.0	21.6	22.4
H ₂ S	1.5	2.4	-	2.3	1.0	-	-	-	-
Oil properties									
Density, 25°C.	1.000	1.060	0.988	1.040	0.952	-	-	-	-
Viscosity, 25°C.	0.515	-	0.003	-	0.129	-	-	-	-
Carbon residue, %	16.1	25.4	13.0	20.6	8.4	-	-	-	-
Unsaturation, %	58	86	74	-	55	-	-	-	-
Sulphur, %	1.7	2.2	-	1.65	0.77	-	-	-	-
Initial B.P. °C.	65	60	60	58	52	65	-	105	55
Per cent. at 200°C.	12	17	19	13	25	14	-	-	19
Per cent. at 300°C.	37	39	41	28	46	-	-	-	45
End point, °C.	343	357	330	335	343	255	-	-	390
Per cent. pitch	36	41	39	41	37	65	-	-	30
Pitch plus coke as per cent. bitumen	16	10	14	16	16	20	-	-	9

which gives the fraction of the original bitumen remaining as pitch or pitch and coke. This figure represents the ultimate residue that is difficult to hydrogenate. It does not include any coke produced in the primary hydrogenation. Coke formation from the bitumen may be suppressed entirely at 425°C. and minimized at 450°C. It is believed that the coke production is largely accidental and originates in substances that are easily decomposed and hydrogenated. The pitches that are produced are very stable and do not decompose at temperatures above 400°C. at atmospheric pressure; whereas cracking always occurs with the oils between 300 and 350°C.

The charges varied from a fluid oil in experiments no 4.1, no. 4.2, no. 5.1 and no. 2.1A to a brittle pitch melting above 200°C. in experiment no 4.3. Pitches that softened between 30°C. and 40°C. were used in no. 2.1 and no. 4.3A. A hard pitch used in no. 2.2 and no. 2.3 melted near 70°C. The asphalt content, as given by the A.S.T.M. method, ranged from 25% in the oils to over 99% in the brittle pitch. The amount of catalyst in the charge as tabled does not take into account any catalyst remaining from previous hydrogenations.

The experiments 4.1 and 4.2 on crude oils less gasoline only require little comment. They show a gasoline production slightly less than that in the preliminary hydrogenation. The loss is rather large in each case and represents a further yield of light oils. Although the oil produced was not as good, the pitch content was much smaller than in the primary hydrogenation. The higher temperature and smaller charge in experiment no. 4.2 reduces the pitch content to the greatest extent. It is interesting to note

the absence of coke formation in both these experiments. Fig. XV shows the pressure-time and pressure temperature curves of experiment no. 4.1. Hydrogen absorption occurs in each cycle but only at a slow rate compared to experiments with fresh bitumen. The material appears very stable and does not crack readily.

Experiment no. 5.1 on a slightly heavier oil residue resembles the above experiment. The hydrogen absorption is, however, nearly three times as great in the latter case which indicates an adverse effect on hydrogenation by the light oils in the charges of experiment no. 4.1 and 4.2. On the other hand the presence of molybdic anhydride in no. 5.1 and the small charge used, may account for the increased hydrogen absorption. The gasoline production is higher and the maximum pressure is lower as would be expected.

Experiments no. 2.1 and 2.1A were successive hydrogenations of the same charge. The first experiment was with a soft pitch residue from vacuum distillation to 250°C. of the lighter crudes of Table II. The second experiment was on the crude oil resulting from the first experiment less the amount required for the ordinary tests. The most notable feature is the constancy of the pitch and coke residue referred to the original bitumen. The pitch content of the charge is decreased only slightly in the second experiment while the gas and coke yield increase greatly. The further production of gasoline is small. The oil obtained in the second experiment was much improved as compared to the charge. The charge, which was the product of experiment no. 2.1, was so viscous that viscosity and unsaturation determinations were

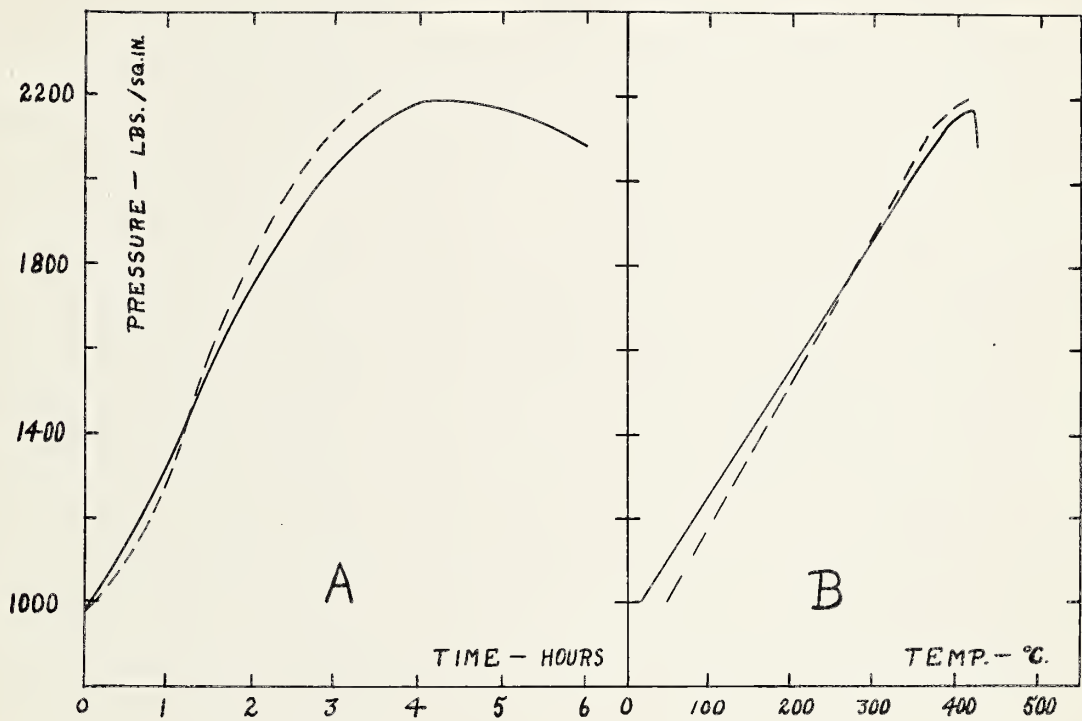


Fig. 15. Experiment No. 4.1, A, Time-Pressure Relations,
B, Temperature-Pressure Relations.

1st. Cycle. _____

2nd. Cycle. _____

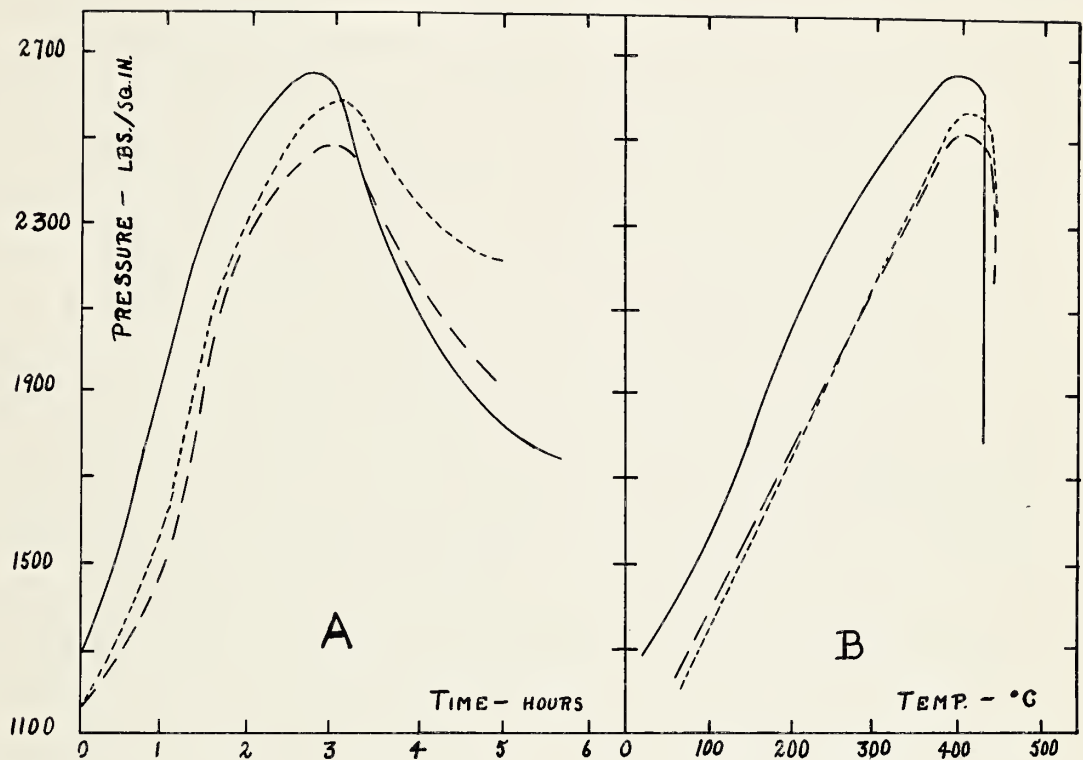


Fig. 16. Experiment No. 2.1A, - A, Time-Pressure Relations,
B, Temperature-Pressure Relations.

1st. Cycle. —————
 2nd. Cycle. - - - - -
 3rd. Cycle. - . - . -

not possible. It would appear that hydrogenation in the second experiment is almost wholly confined to the oil and does not effect materially the asphaltic substances. The similarity of this reaction to the hydrogenation of bitumen is brought out by an examination of the pressure-time and pressure-temperature curves of Fig. XVI for experiment no. 2.1A. They differ remarkably from the curves of Fig. XV in regard to rate and extent of hydrogen absorption.

Experiment no. 2.2 was carried out with a small charge of hard pitch from the heavier crudes of Table II. A higher temperature and a catalyst were employed in an endeavour to reduce the pitch residue. Hydrogen absorption was rapid and large, but coke and gas production were very great. The product was a mixture of viscous pitch and lump coke. A small quantity of water was formed and the odour of ammonia was very noticeable. The proportions of oil and coke are very approximate and the large loss unavoidable, because of the difficulty in removing the product from the autoclave. The liquid portion was very unstable and commenced to crack at 240°C. on distillation. Cracking ceased at 255°C. with 35% over. The remainder was a brittle pitch of very high boiling point. This experiment shows strikingly the resistance of part of the asphaltic material in the bitumen to hydrogenation. Apparently destructive cracking of the asphalt will occur before hydrogenation begins. It is noteworthy that water has not been found in the products of any previous experiment and ammonia has been only noticed in traces. These facts would indicate a deep seated change in the nature of the reactions in this experiment.

Experiment no. 4.3 on a very brittle pitch illustrates the great stability of these residual asphaltic materials. No hydrocarbons soluble in gasoline were present in this charge. No oil or coke production occurred on hydrogenation with molybdic anhydride at 450°C . The hydrogen absorption was real and the high loss was due to material left in the autoclave. The recovered material was very viscous and sticky. Its softening point was about 30°C . and its initial boiling point was above 200°C . The product of experiment no. 4.3 was subjected to hydrogenation again in experiment 4.3A at 500°C . A large hydrogen absorption occurred and the product was distinctly more fluid than the charge. A small amount of finely divided coke was suspended in the liquid. Considerable water, from 5 to 7 c.cms., and ammonia were formed. The liquid was still viscous and extraordinarily sticky and tenacious. Distillation was impossible on account of extensive foaming of the liquid into the condenser and receiver. Repeated trials did not reduce the foaming to any extent. The initial boiling point of 105°C . tabled is probably too high.

The last experiment, no 2.3, on a hard pitch as used in no. 2.2 was carried out with aluminium chloride as catalyst. This catalyst is more destructive in its action than molybdic anhydride and the results confirm this in showing a degree of success as compared to experiment no. 2.2. The coke product was not very different in amount but appeared in a finely divided form. Water was produced in small quantities and was acidic in nature. Considerable of hydrogen chloride was present in the gas and oil. The oil was quite

fluid and yielded gasoline amounting to 14 per cent. of the charge. Its behaviour on distillation was very interesting. A small amount of cracking occurred at 300°C. and then ceased. Boiling continued quietly thereafter, even when the still was above 450°C. and the still head recorded a temperature of 390°C. The distillate above 300°C. resembled the red oil of coal tar in appearance and odour but contained paraffin wax. The residue from this distillation formed, on cooling, a brittle coal like substance, melting above 200°C. It may be of interest to mention that the behaviour of this oil above 250°C. is similar to that of the oils boiling in the same temperature range obtained in the hydrogenation of Alberta coals.

Considering the results of this series of experiments as a whole, it is probable that 75% of Alberta bitumen may be converted easily to gasoline and oil. Of the remainder, 10 per cent. appears as gaseous hydrocarbons and the other 15 per cent. of asphaltic material is very resistant to both cracking and hydrogenation. Experiment no. 2.3 shows that a proper catalyst offers hope in reducing this material. Another and promising possibility is afforded by the anomalous result recorded in experiment no. 4.2. The pitch residue has been reduced in this instance to 10 per cent. of the original bitumen by hydrogenation at 450°C. of an oil containing considerable non-asphaltic material. The significance of this result will be determined by further work on residues of various initial boiling points and by experiments in an apparatus that will allow of continuous removal of the gasoline fraction as formed.

The hydrogen absorption in the last three experiments when considered with the hydrogen absorption in the primary experiments, shows a total absorption by the bitumen of 3 per cent. or more. Part of this appears in the gaseous hydrocarbons but nevertheless, this figure shows definitely that the theoretical capacity of the bitumen is not very much greater than its practical capacity for hydrogen.

Summary:

From the results reported, several conclusions are evident in regards to the hydrogenation of Fort McMurray bitumen.

That hydrogenation of the larger part of the bitumen proceeds with ease and commences at comparatively low temperatures has been demonstrated. Further, the rate of hydrogenation is very dependent on the temperature, the presence of a catalyst, and the previous extent of hydrogenation. Reaction commences slowly at 200°C. and increases in rate with rising temperature. The presence of molybdic anhydride doubled, approximately, the rate of reaction. The extent and speed of hydrogenation decreases with successive treatments of the same lot of bitumen due to the adverse effect of an increasing proportion of simple hydrocarbons.

An increase in the relative amount of hydrogen to bitumen in the autoclave has the effect of increasing the absolute rate of reaction and the degree of hydrogenation possible in one treatment. In consequence of the shorter time required, coke formation is largely suppressed.

The optimum temperature for use in a static apparatus is not less than 425°C. nor more than 450°C. Rapid hydrogenation and little coke formation occur in this temperature range.

Experiments on distillation residues from hydrogenated bitumen reveal the presence in this bitumen of a small and very stable asphaltic fraction. This material has not been hydrogenated without excessive coke formation but the problem does not appear to be insoluble. It may

be that a higher temperature will be necessary and as a consequence, two reaction chambers.

The occurrence of two co-existent equilibria has been assumed in an attempt to account for the course of the reactions in the autoclave. One reaction is between bitumen and hydrogen, and the products of hydrogenation. The other is between bitumen and gaseous hydrocarbons, and the products of cracking. An increasing temperature favours the latter reaction more than the former. Careful temperature control is essential in the prevention of coke formation through the second reaction.

The mechanism of the reaction of hydrogen with the bitumen would seem to consist of an addition of hydrogen to the unsaturated linkages produced by thermal decomposition of the complex carbonaceous materials.

PART III.

The following section deals with the preliminary work on the hydrogenation of some Alberta coals. This work has not progressed beyond the stage of development leading to a satisfactory technique.

The mechanical and chemical properties of coal are very different from those of bitumen and the same methods do not apply to both. Early experiments in the Cook autoclave revealed these differences strikingly. In the first place the coal could not be treated satisfactorily in its dry form because of coking. A liquid medium in which the coal could be suspended was required. Various materials were used such as bitumen, hydrogenated bitumen, liquid petrolatum, crude petroleum and phenol. No satisfactory results could be obtained because the coal invariably settled and caked in the autoclave in spite of the stirrer. Severe local superheating developed under these conditions, and pressures in excess of the capacity of the autoclave developed.

The work was transferred to the second and larger autoclave described in Part II. The experiments in this autoclave were satisfactory from the mechanical point of view and have dealt largely with the discovery of a satisfactory liquid medium to carry the coal. Three materials have been examined; residual oils after distillation of the crude oils from the hydrogenation of bitumen, phenol and tetrahydronaphthalene (tetralin).

The latter substance has proved to be of considerable interest and shows promise of yielding valuable results. It is readily dehydrogenated to naphthalene and can just as readily be reformed or hydrogenated to decahydronaphthalene, (decalin). These reactions occur in the autoclave and all three materials are recovered. At the same time 70% of the coal is converted to oil and tar and a large hydrogen absorption occurs. The evidence leads to the belief that tetralin acts in the manner of a hydrogen carrier and a good coal solvent.

Materials:

Of a series of typical Alberta coals supplied by Prof. E. Stansfield of the Research Council of Alberta, three individuals have been used to date in experiment. The origin, analysis and classification of these three coals are given in Table VIII.

The first suspension medium employed was the residual oil from the distillation to 225°C. of hydrogenated McMurray bitumen. Phenol of Mercks' U.S.P. grade was next used. The third suspension medium was Eastman grade tetralin, B.P. 202 - 204°C.

Commercial electrolytic hydrogen and Viking natural gas were used as in previous work. Only three catalysts have been used, namely, ammonium molybdate, molybdic anhydride and ferric oxide. They were ground to pass 100 mesh screens and incorporated with the coal and suspension medium.

Apparatus:

The apparatus and its arrangement was identical in all respects with the set up described in Part II.

T A B L E V I I I

HYDROGENATION OF ALBERTA COAL - ANALYSES OF COALS AS RECEIVED

Sample	Moisture	Ash	Volatile Matter	Fixed C.	Nitrogen	Sulphur	Classification
419-29 McLeod River Collieries	6.20	10.10	38.3	45.4	0.6	0.5	Sub. Bituminous.
420-29 Mine 295 Pincher Creek	2.18	9.26	32.5	56.1	0.9	0.8	Bituminous
424-29 Mine 678 Drumheller	15.21	8.20	31.4	-	-	-	Lignite

Procedure:

A ground sample of coal was suspended in a definite amount of the liquid medium under investigation. A sufficient amount of catalyst, usually 5% by weight, was incorporated thoroughly into the resulting paste. The charge, varying in weight from 300 to 900 gms. in different experiments was then transferred to the clean autoclave. After closing and washing out any trapped air with methane, the system was tested for leaks by raising the methane pressure to the vicinity of 2000 lbs. per sq. in. If tight, this methane was released and hydrogen added to the desired initial pressure. Runs were made at temperatures varying from 425°C. to 475°C. for time intervals in the vicinity of four hours. As in the experiments with tar, temperature and pressure were recorded continuously. Rocking of the machine was commenced at about 100°C. when the charge was usually quite fluid.

At the end of an experiment the cooled gas was liberated through a wet test gas meter to a gasholder. After reaching a uniform composition this was later analyzed. Upon occasion two charcoal absorbers in series were inserted ahead of the meter to recover any low boiling hydrocarbons that might be present in the exit gases. The recovery here was usually very small, averaging about 2-4 gms. per cycle. In the majority of these experiments a second addition of hydrogen was made to the coal. In a few cases experiments of more cycles were conducted. And on one occasion only one addition was made. This latter procedure also held where natural gas was substituted for hydrogen.

After opening the autoclave the resulting oily paste

was treated in a variety of ways depending a good deal on the nature of the suspending medium. Where residual oils were used separation by draining proved sufficient. In those cases in which phenol and tetralin were employed various organic solvents were required. The most common method in the phenol experiments was alcohol extraction. This left the unchanged coal which was then dried and weighed. Low temperature distillation of the extracted liquid yielded the alcohol and any low boiling products of reaction, which were not separated. Extraction of the residual oil with petroleum ether and carbon disulphide yielded two fractions. These last separations were not very efficient and gave little information as to the true nature of the reaction products. Substantial decreases in the weight of the coal used were the best indications of reaction.

The products of hydrogenation in the presence of tetralin lent themselves more readily to separation. The autoclave paste was first heated to 125°C . in an oil bath to rid it of any low boiling hydrocarbons and water present. This product was recombined with the low boiling oils later separated. Extraction of the remaining paste with ether was carried out and the solid residue dried and weighed. The weight of this residue less the weight of the catalyst was taken to represent the unchanged coal. The ether solution was distilled in a small fractionating column and all the ether collected below 75°C . The preliminary treatment of the autoclave product in an oil bath at 125°C . ensured that no low boiling products would be present in the ether solution. After the removal of the ether, distillation was continued until the residue was reduced to pitch or coke.

Results and Discussion:

In Table IX are given the details of three experiments on the hydrogenation of coal using tar residues as the suspension agent. This solvent proved to be entirely unsatisfactory. As far as could be determined the coal was recovered after experiment in an unchanged condition. A considerable cracking to coke of this oily material always occurred. As a result it was quite impossible to accurately weigh the coal after reaction. In all cases the amount of recovered oil was far less than that originally used. Hydrogenation of the coal was considered to be negligible. The course of these experiments is best followed by the time-pressure and temperature-pressure records, given in Fig. XVII for experiment no. 96. Two additions of hydrogen were made in this case. The pressure during the first cycle built up steadily with time. In the second it reached a constant steady value after the fourth hour. Reaction was evidently quite complete under these conditions. The temperature-pressure relations do not show the sharp downward slope that indicates a large hydrogen absorption. It is probable that a large percentage of the oily suspending medium was gaseous under existing reaction conditions. The coal was left in a more or less dry state and was unaffected by the hydrogen present. To inquire into the possibilities of the addition of hydrogen to coal alone, two additions of hydrogen were made to 900 gms. of the ground coal. The fact that no liquefaction occurred and that the coal was recovered in an apparently unchanged state, would support the above hypothesis. Only about 0.4% of hydrogen was absorbed and the

T A B L E I X

HYDROGENATION OF COAL - SUSPENDING MEDIUM - TAR RESIDUES

Experiment	94	95	96	97
Coal no.	424-29	424-29	424-29	424-29
Wt. coal in gms.	450	450	450	370
Wt. solvent in gms.	550	450	450	-
Catalyst %	nil	nil	(NH ₄) ₂ ^{5%} MoO ₄	(NH ₄) ₂ ^{5%} MoO ₄
No. of cycles	1	1	2	2
Time/cycle in hrs.	3	3	3	1
Ave. Temp. °C.	425	425	425	345
Ave. Initial Pressure in lbs./sq. in	745	745	720	1030
Ave. Maximum Pressure	3585	3240	3195	3370
Ave. Final Pressure	930	890	745	990
Ave. Pressure drop	-185	-145	-25	40
H. absorbed %	0.1	0.2	0.4	0.4
Gas yield in litres 1 Kg. charge	59.8	61.4	127.3	78.0
% charge to oil	-	14.5	13.3	nil
% charge to coke	-	65.7	67.3	87.6
% charge to gas	3.4	3.0	5.6	4.7
% charge to loss		16.8	13.8	7.7
Gas % -				
CO ₂	11.8	15.9	13.2	15.4
CnH _{2n}	1.6	1.8	1.5	0.7
H ₂	33.8	31.1	34.8	60.3
CO	0.9	1.6	1.3	0.8
C ₂ H ₆	22.2	18.7	22.3	6.1
CH ₄	23.2	16.9	16.4	11.8

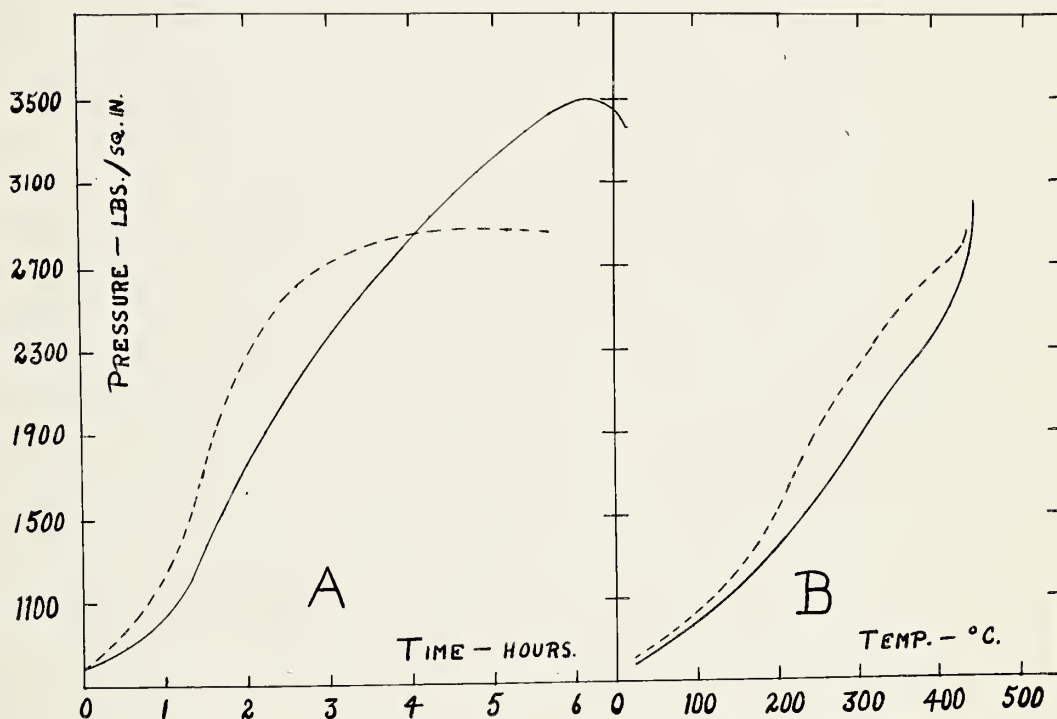


FIG. 17. Experiment No. 96. A, Time-Pressure Relations,
B, Temperature-Pressure Relations.

1st. Cycle. _____

2nd. Cycle. _____

pressure rose to a surprising extent at a temperature so low as 350°C.

The use of phenol as a solvent for the coal in this work lead to more favourable results. Five experiments employing this technique are reported in Table X. As before, two additions of hydrogen were made to the coal at temperatures around 425°C. In the latter two of these experiments it was deemed advisable to reduce the weight of the charge from 900 to 400 gms. in order to raise the hydrogen concentration in the reaction mixture. A higher hydrogen absorption by the charge and a higher percentage coal conversion resulted from this procedure. Consequently it was adhered to in all subsequent work. There was no doubt from these experiments that a certain amount of the coals were changed by hydrogenation. Thus in experiment no. 102, 21.4% of the coal was converted to alcohol soluble products and as high as three per cent. by weight of hydrogen was absorbed, presumably by the coal. The pressure drop after each hydrogen addition was always quite noticeable. The course of the pressure is shown graphically in Fig. XVIII and indicates beyond doubt a large hydrogen absorption. The time-pressure relations, curves A, show a rapid hydrogen absorption after the first three hours of heating. The temperature-pressure curves, B, fix this initial reaction temperature as being between 400°C. and 425°C. At lower temperatures the pressure built up steadily with time indicating very little hydrogen absorption. Coals differ essentially from bitumen in this respect and the result suggests that hydrogenation does not occur until some thermal decomposition has taken place. In all of these experiments,

TABLE X

HYDROGENATION OF COAL - PHENOL AS SUSPENDING AGENT

Experiment no.	98	99	100	101	102
Coal no.	424-29	424-29	419-29	419-29	419-29
Wt. coal in gms.	333	355	360	200	210
Wt. solvent in gms.	317	355	360	200	220
Catalyst %		5%	5%	5%	5%
	nil	$(\text{NH}_4)_2\text{MoO}_4$	$(\text{NH}_4)_2\text{MoO}_4$	$(\text{NH}_4)_2\text{MoO}_4$	$(\text{NH}_4)_2\text{MoO}_4$
No. of cycles	2	2	2	2	2
Time/ cycle in hrs.	3	3.5	4	4	4
Ave. Temp. °C.	425	425	425	425	425
Ave. Initial Pressure in lbs./sq. in.	720	745	765	790	810
Ave. Maximum Pressure	2570	2740	2570	2285	2290
Ave. Final Pressure	665	550	610	600	550
Ave. Pressure drop	55	195	155	190	260
H. absorbed %	1.8	2.0	1.0	3.1	2.5
Gas yield in litres					
Kg. charge.	71.3	88.4	64.2	64.1	95.3
% charge to oil	40.0	37.8	44.2	47.6	47.8
% charge to coke	45.4	48.0	43.2	41.7	36.6
% charge to gas	6.2	7.9	6.6	5.4	8.4
% charge loss	8.4	6.3	6.0	5.3	7.2
Gas % -					
CO ₂	15.5	14.8	12.6	5.6	5.7
CnH _{2n}	0.6	0.7	0.2	0.3	0.6
H ₂	43.4	35.1	53.5	77.9	63.3
CO	3.8	0.6	0.7	0.9	1.5
C ₂ H ₆	5.3	2.9	7.1	3.3	6.2
CH ₄	21.5	34.4	22.4	10.3	16.1
% coal converted	11.4	0.5	10.8	12.5	21.4

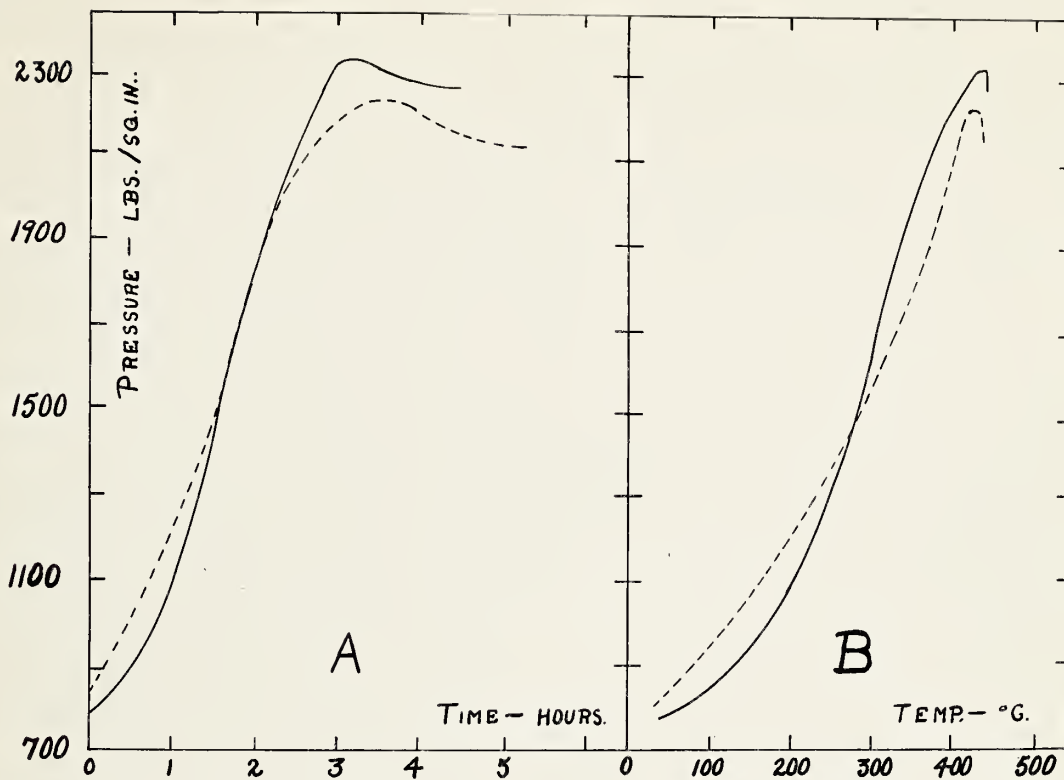


Fig. 18. Experiment No. 101 . Time-Pressure Relations,
B, Temperature-Pressure Relations.

1st. Cycle. _____

2nd. Cycle. _____

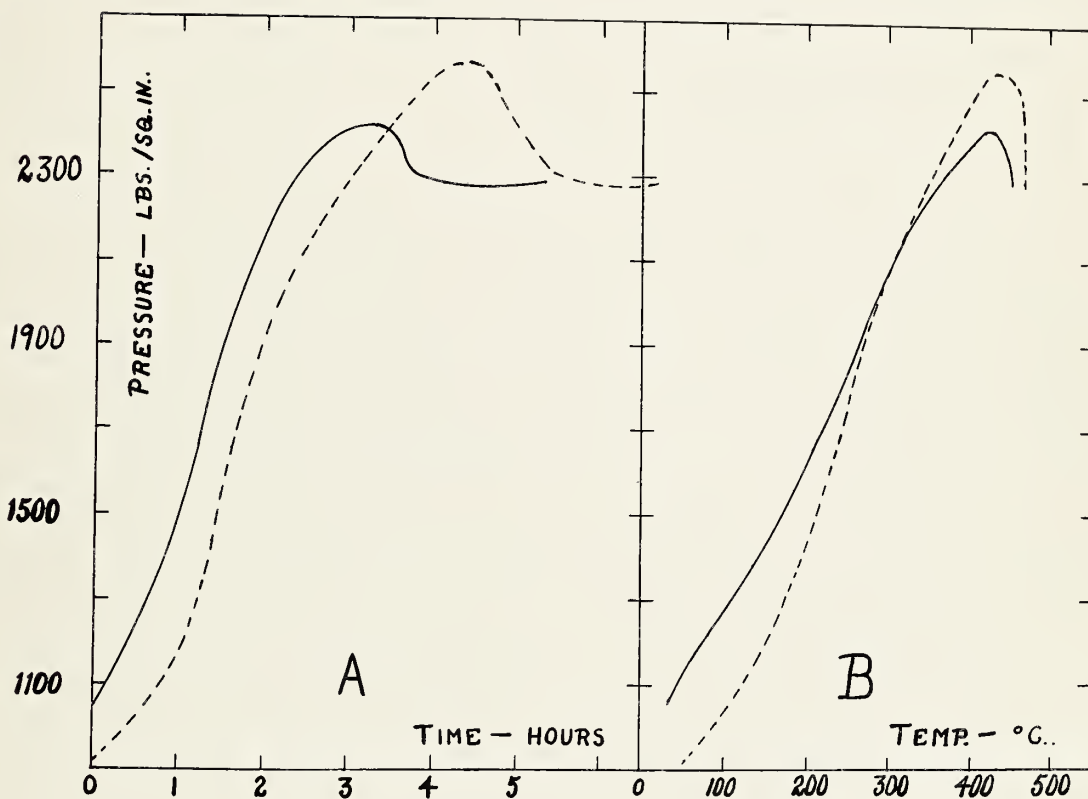




Fig. 19. Experiment No. 110:- A : Time-Pressure Relations B, Temperatur
-Pressure Relations.

1. 
2. 

however, trouble was experienced in separating the oily reaction products. Extraction with alcohol of the sticky paste allowed the recovery of any unchanged coal in its entirety. But the use of secondary solvents to the alcohol in separating the organic reaction products proved unsatisfactory. The final products of such a technique were never free from phenol: which fact precluded the collection of any quantitative data in regards to these oils. It was finally decided that a complete knowledge of the action of hydrogen on coal, was not forthcoming from experiments, in which phenol was employed as a suspension agent for the coal.

In Table XI are recorded the data of six experiments in which the coal was impregnated with tetrahydronaphthalene, or tetralin, as it is commonly called. This solvent acted in a very favourable manner and a conversion of 77% of the coal to ether soluble products is reported. The reaction paste from this work was in every case quite fluid and contained finely divided coal or coke in suspension. Removal from the autoclave was effected with great ease. Hydrogen absorption was usually high - 6% by weight being taken up by the coal in experiment no. 112 after four additions were made. In spite of a reaction temperature of 450°C. maximum pressures were never excessively high. Substantial pressure drops were noted even after the last addition in those experiments of four cycles mentioned above. These facts are best illustrated graphically and in Fig. XIX, experiment no. 110 is given as a typical example. Pressure drops with time are much more sharply defined in these curves than in previous work with coal. The optimum temperature of reaction under

TABLE XI

HYDROGENATION OF COAL - TETRALIN AS SUSPENDING AGENT

Experiment no.	103	110	112	119	120	121
Coal no.	419-29	419-29	419-29	420-29	420-29	420-29
Wt. Coal in gms.	200	240	252	200	206	200
Wt. solvent in gms.	200	120	127	109	106	100
Catalyst %	5%	5%	5%	5%	5%	5%
	(NH ₄) ₂ MoO ₄	MoO ₃	MoO ₃	MoO ₃	MoO ₃	Fe ₂ O ₃
No. of cycles	2	2	4	1	4	2
Time/ cycle in hrs.	3.5	4	4	1	4	3
Ave. temp. °C.	450	450	450	450	450	450
Ave. Initial Pressure in lbs./sq. in.	965	965	1075	1235	1160	1120
Ave. Maximum Pressure	2335	2500	2665	2625	2820	2455
Ave. Final Pressure	470	585	665	670	875	765
Ave. Pressure drop	495	380	410	565	315	355
H. absorbed %	4.1	3.3	6.1	2.8	5.6	3.3
Gas yield in litres						
Kg. charge	82.3	145.9	175.7	51.7	216.8	122.6
% charge to oil	76.3	67.0	55.0	66.6	59.4	56.8
% charge to coke	15.0	16.3	15.8	21.6	16.8	22.8
% charge to gas	3.2	8.0	7.3	1.7	7.5	5.0
% loss	5.5	8.7	21.9	10.1	16.3	15.4
Gas % -						
CO ₂	3.9	5.1	2.4	0.4	0.3	1.1
CnHgn	0.8	0.9	0.6	0.5	0.3	0.5
H ₂	70.0	58.9	74.2	76.4	80.2	75.8
CO	1.1	2.9	0.9	1.1	0.9	0.9
C ₂ H ₆	2.8	12.2	5.8	3.0	4.0	5.5
CH ₄	16.1	16.0	9.7	11.6	6.8	9.6
% coal converted	72.8	76.2	76.8	65.0	73.4	64.0
% charge to oil -						
1. Below 175°C.	-	12.1	19.5	9.0	11.6	7.3
2. 175 - 225°C.	-	30.3	18.3	29.6	26.3	25.7
3. 225 - 350°C.	-	5.5	3.0	13.0	7.0	5.1
4. Pitch	-	6.6	7.0	8.3	7.6	14.9
Dist. Loss %	-	12.5	7.2	6.7	6.9	3.4

these conditions would seem to be in the neighborhood of 430 - 450°C. according to the relations exhibited in B. Fig. XIX.

A very complex oil resulted from the ether extraction of the autoclave paste. Distillation was resorted to in order to evaluate these products. Four fractions were usually separated. The first fraction, boiling below 175°C., included that part recovered in the initial treatment at 125°C. before ether extraction. The larger part of this came over below 100°C., the temperature rapidly climbing after this point had been reached. This liquid always separated into two layers, the lower being largely water and the upper a light straw yellow oil. The water produced amounted to 5 to 10% of the original coal and was acidic. The oil layer included those substances boiling below 175°C. and some higher boiling compounds carried over with the water by steam distillation. There was also present in this layer low boiling acidic substances, probably of an organic nature.

The fraction boiling between 175°C. and 225°C. consisted largely of unchanged tetralin and naphthalene, their proportions depending upon the nature of the experiment. The greater the hydrogen absorption recorded the less was the proportion of naphthalene. A decided yellow tinge in this fraction indicated the presence of other substances besides naphthalene, tetralin and decalin. Separation of these was not accomplished.

Above 225°C. three fractions were collected. The first was a heavy yellow oil of apparently high lubricating value. The second oil, isolated on occasion, consisted of the same oil with some white wax-like crystals. The last

fraction, from 350°C. to the end, was a heavy red oil, which darkened on standing. The amount of this last fraction depended on the temperature to which distillation was carried. In all cases a stable pitch amounting to 5% of the original coal remained in the distilling flask. This pitch boiled quietly without decomposition at temperatures as high as 450°C. yielding further amounts of red oil. On cooling it solidified around 200°C. and had the appearance of anthracite coal. The appearance of crystals of naphthalene in the ether soluble products of these experiments points to the theory that the tetralin was dehydrogenated to naphthalene in the presence of the coal under these working conditions. In so doing it hydrogenated the coal, behaving as a catalyst or hydrogen carrier. This theory is supported by the fact that in no case was the amount of hydrogen excessively high in subsequent gas analyses.

To further study the action of hydrogen in Alberta coals in the presence of tetralin, experiments were run in which the coal paste was heated to 450°C. under high methane pressures. A study of Table XII will show that liquefaction of the coal undoubtedly occurred under these conditions. Only 5 per cent. of the coal was recovered in an unchanged condition after reaction. No tetralin appeared as such in the resulting autoclave paste. Large amounts of naphthalene crystals were obtained by distillation. Subsequent analysis showed no great excess of hydrogen in the gaseous products of reaction. The coal had been evidently hydrogenated at the expense of the tetralin under these experimental conditions and solution of the coal did not play a predominating

T A B L E X I I
HYDROGENATION OF COAL BY TETRALIN
IN PRESENCE OF HIGH PRESSURES OF METHANE.

Experiment no.	111	113
Coal no.	419-29	419-29
Wt. Coal in gms.	253	200
Wt. Solvent in gms.	133	207
Catalyst %	2.5%	5%
	MoO ₃	MoO ₃
No. of cycles	1	1
Time/cycle in hrs.	3	4
Ave. Temp. °C.	450	450
Ave. Initial Pressure in lbs./sq. in.	390	480
Ave. Maximum Pressure	1730	1970
Ave. Final Pressure	580	720
Ave. Pressure drop	-190	-240
H. absorbed %	-	-
Gas yield in litres		
1 Kg. charge	29.6	78.0
% charge to oil	40.0	57.7
% charge to coke	43.5	24.3
% charge to gas	0.3	1.4
% loss	16.2	16.6
Gas %		
Co ₂	7.9	5.6
CnH _{2n}	1.2	0.8
H ₂	7.4	8.0
CO	3.3	1.1
C ₂ H ₆	11.9	7.3
CH ₄	62.6	65.2
% coal converted	34.3	49.8
% charge to oil:		
1. Below 175°C.	2.0	0.5
2. 175-225°C.	24.8	36.6
3. 225-350°C.	3.5	-
4. Pitch	1.3	6.8
% Distillation Loss	8.4	13.8

part. The ether-soluble oil resulting was readily divided into much the same fractions as before. A certain amount of water appeared in the first fraction. Between 175°C . and 225°C . solid naphthalene crystals appeared in the receiving cylinders. At higher temperatures the usual yellow and red oils appeared. A heavy black pitch remained. In Fig. XX one of these reactions (experiment no. 113) is followed graphically. These curves differ a good deal from the usual hydrogenation reactions. The pressure rises steadily and shows no tendency to drop. The theory that tetralin acts as an hydrogenating agent would predict this behaviour. The volume of the naphthalene and its vapour pressure are not very different from those of the tetralin supplying the hydrogen.

Figure 20.

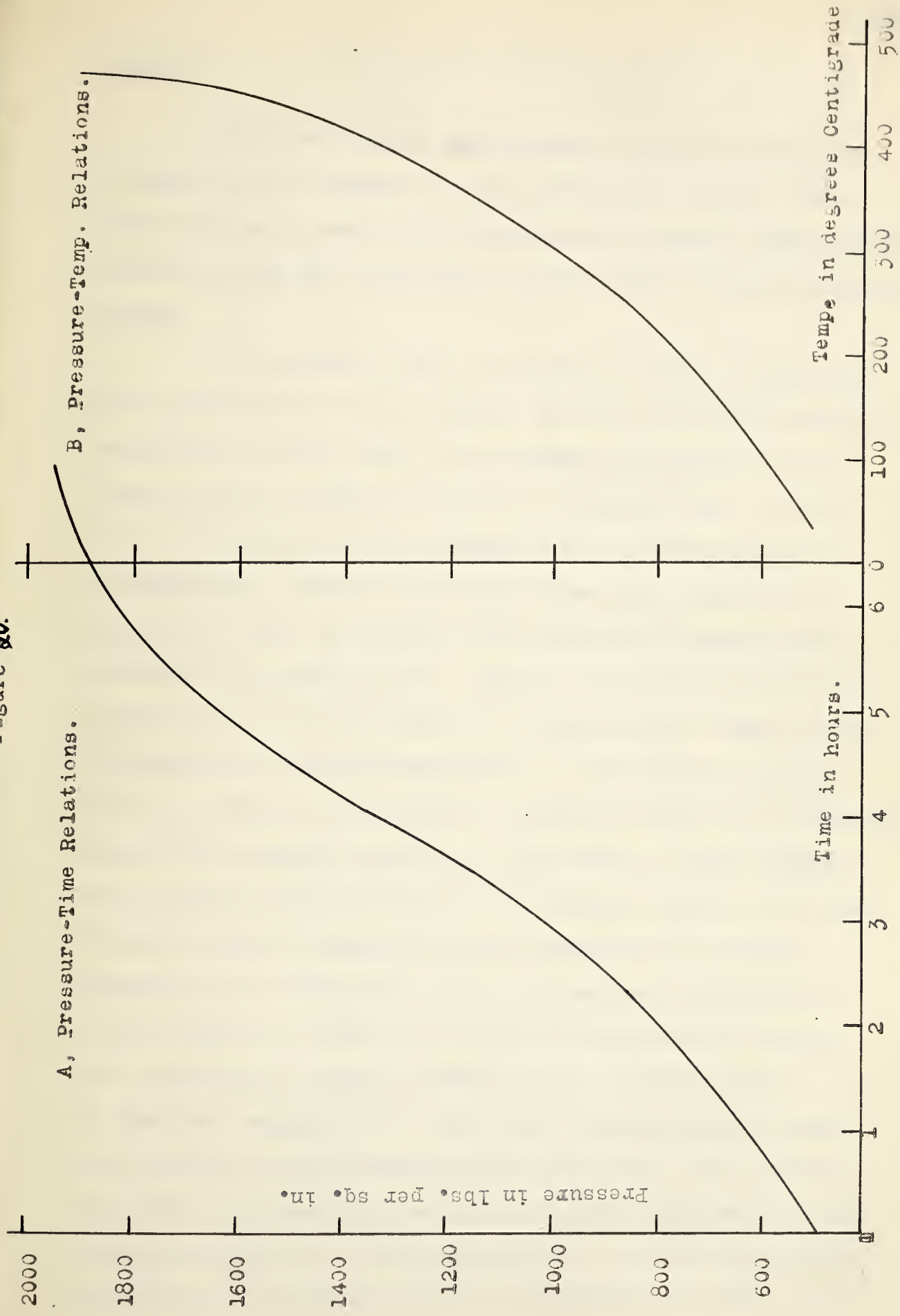


Fig. XV.

Summary:

These preliminary experiments on the hydrogenation of coals are of interest for two principal reasons. They show that the Alberta coals examined are readily hydrogenated. They show also the importance of the nature of the suspension medium.

It is obvious that a suspension medium is necessary, if a reasonable rate of reaction is to be obtained, from the experiment on coal alone. The chemical properties of the medium control largely the rate of hydrogenation. An oil such as results from the hydrogenation of bitumen is unsatisfactory. Phenol is of some value and tetralin is superior in that it produces very rapid and extensive reduction of the coal to oil. Roughly speaking, the order of effectiveness of the medium is in the order of their ease of hydrogenation and dehydrogenation. The evidence suggests that the action of the medium is primarily that of a hydrogen carrier by chemical reaction. The medium no doubt assists the reaction by solution of both hydrogen and coal, but this function does not appear to be as important as usually assumed in the literature. In the presence of palladium black tetralin is known to be an able hydrogenating agent for a variety of organic acids and some terpenes (28). It has been suggested for use in the hydrogenation of coal as a surface tension reducing agent (29) but it is believed here that the beneficial action is due in large part to the tetralin acting as a hydrogen carrier. Tetralin is readily prepared by the hydrogenation of naphthalene at 200°C. and

is just as readily decomposed at higher temperatures (30).

There is an obvious field for further work in the examination of other compounds capable of reversible hydrogenation as suspension media in this work.

The use of one part of tetralin to two parts of coal in the hydrogenation process results in the reduction of 75% of the coal to ether soluble products; an effectiveness three times as great as that of phenol. Temperatures from 425°C. to 450°C. appear to be satisfactory. The maintenance of a high hydrogen concentration is necessary in view of the improved results obtained with small charges in the autoclave.

- The products of hydrogenation are largely high boiling oils and tar. The light oil yield is small. Further hydrogenation of the heavy oils needs investigation and would result in larger light oil yields.

The oxygen content of the coal appears for the most part as water indicating the hydrogenation of hydroxyl and carboxyl groups. Considerable carbon dioxide also appears and no doubt arises from thermal decomposition at carboxyl groups. Considerable carbon dioxide also appears and no doubt arises from thermal decomposition at carboxyl groups. The acidity of the water fraction suggests the occurrence of stable acids in the coal. The ease of reduction of these hydroxyl and carboxyl groups lends support to reports that water gas is suitable for the preliminary hydrogenation of coal. Its use would result in a considerable saving of hydrogen if carbon monoxide were capable of reducing the oxygen in coal.

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